Compatibility of Hydrocarbon Fuels with Booster Engine Combustion Chamber Liners

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This paper presents the results of material compatability experiments using Mil-Spec RP-1, *n*-dodecane, propane, and methane fuels in contact with OFHC, NASA-Z, and ZrCu coppers. The objectives of the current research are 1) to define the corrosive interaction process that occurs between hydrocarbon fuels and copper combustion chamber liner materials, and 2) to develop and demonstrate protective measures against this corrosive process. Two distinct test methods were employed. Static tests, in which copper coupons were exposed to fuel for long durations at constant temperature and pressure, were used to provide compatability data in precisely controlled environments. Dynamic tests, using the Aerojet Carbothermal Test Facility, were used to expose copper specimens to fuel under realistic booster engine service conditions. Tests were conducted using 1) very pure grades of each fuel and 2) fuels to which a contaminant was added to define the role played by fuel impurities. The findings from metallurgical and chemical analyses of the copper specimens and chemical analysis of the hydrocarbon fuels are provided. Conclusions are reached as to corrosion mechanisms and effects, methods for the elimination of these mechanisms, selection of copper alloy combustion chamber liner and materials, and hydrocarbon fuel specifications as related to advanced booster engine systems.

I. Background

THE selection of the fuel for new liquid oxygen/hydrocarbon gas generator cycle booster engines is one of the most important remaining technical issues. Three fuels are currently under consideration, RP-1, methane, and propane. RP-1 offers the advantages of density and an in-place design data base. Methane offers the advantages of higher specific impulse and lower cost. Propane offers compromise of density, performance, and cost. Fuel selection should be based on the comparative characteristics of the fuels and their impact on engine design, operation, and cost of payload in orbit. The engine designer must have a detailed properties data base for the selected fuel. This data base must cover such issues as combustion characteristics at gas generator and main chamber conditions, cooling capability, and materials compatibility, in addition to the usual physical, chemical, and propellant properties. The potential for corrosive interaction between copper and the candidate hydrocarbon fuels in the cooling channels of the booster engine chamber is a very important issue affecting chamber life and engine performance.

Thermally induced decomposition of the hydrocarbon fuel may result in the deposition of activated pyrolytic carbon on the hot copper channel wall by the flowing coolant, thereby reducing the operational life of the chamber. The inhibition of the pyrolytic decomposition of the hydrocarbon fuel plays a vital role in preventing this postulated corrosion process.

Another corrosion process may be postulated based on the impurities that are present in the fuel. Copper is attacked rapidly by sulfur-containing compounds at elevated temperatures, i.e.,
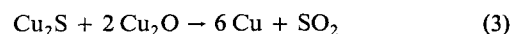
$$2\,Cu + CH_3SH \rightarrow Cu_2S + CH_4 \qquad (1)$$
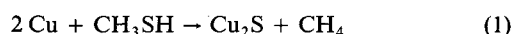
Oxygen reacts similarly, i.e.,
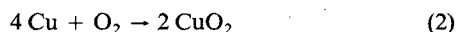
$$4\,Cu + O_2 \rightarrow 2\,CuO_2 \qquad (2)$$

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Cuprous sulfide and cuprous oxide react to form copper, i.e.,

$$Cu_2S + 2\,Cu_2O \rightarrow 6\,Cu + SO_2 \qquad (3)$$

The sulfidation and oxidation of the copper channel wall, acting separately or in concert, result in the formation of a weakened layer that is scrubbed off by the flowing coolant.

Concern about hydrocarbon fuel/combustion chamber liner materials compatibility was sharply focused by previous studies.[1-3] These studies were primarily focused on determining the cooling capability of RP-1, propane, and methane using the electrically heated tube test with OFHC copper bimetallic tubes. Spadaccini et al.[1,2] encountered both copper corrosion and carbon deposition in its studies, while Morinoshi and Cook[3] encountered copper corrosion and no carbon deposition.

The electrically heated tube test is accepted as a proper test method for the determination of the cooling capability of candidate propellants, e.g., to develop a heat transfer correlation for each propellant over a representative range of heat flux, temperature, and velocity. It was not developed to determine, i.e., measure and understand, the compatibility of candidate propellants with candidate materials under engine operating conditions. Indeed, the determination of cooling capability is predicated on smooth tube walls throughout the duration of the test. The assumption is made that the propellant does not react with the tube wall, i.e., wall roughening, caused by corrosion and/or other processes, does not occur. The electrically heated tube test does not provide a realistic simulation of the environment that actually exists in the cooling channel of a booster engine chamber.

With this background, the current research was undertaken to study the compatibility of hydrocarbon fuels with copper alloys. The objectives of this program are 1) to define the corrosive process that occurs between hydrocarbon fuels and copper combustion chamber liner materials using test methods that do not depend on direct electrical heating and 2) to develop and demonstrate protective measures against this corrosive process. This paper presents the experimental results that address the first of these two objectives. A description of the test methods and conditions is followed by a discussion of the significant findings obtained from testing each of the hydrocarbon fuels and copper materials used in the program.

II. Test Methods

Static Test Methods

Two static test methods were used to study the compatibility of the hydrocarbon fuels with copper, i.e., the sealed glass ampule test for RP-1 and n-dodecane, and the Aminco bomb test for methane and propane. In the sealed glass ampule test, the fuel and copper coupon were placed in the ampule (Fig. 1) under precisely controlled conditions, sealed, and heated to 204°C (400°F) in a constant-temperature oven for 14 days. After exposure, the pressure in the ampule was measured, and the liquid and gas phases were analyzed for hydrogen and hydrocarbons using gas chromatographic techniques. The coupons were weighed and examined with optical and scanning electron microscopes.

In the Aminco bomb test, the fuel and copper coupon were placed in the bomb, brought to temperature, e.g., 343°C (650°F), and pressure, e.g., 20.7 MPa (3000 psia), for 30 min, and cooled. The total test time was approximately 5 h. After exposure, the contents of the bomb were analyzed as before.

The sealed glass ampule test offers the advantage of visual observation of the fuel/specimen sample throughout the course of the test, but its applicability is limited to comparatively nonvolatile fuels, e.g., RP-1 and n-dodecane. The Aminco bomb test offers the advantage of testing at high pressure, but it is best suited to the evaluation of comparatively volatile fuels, e.g., methane and propane.

Dynamic Test Method

Dynamic tests were conducted in the Aerojet Carbothermal Test Facility with four hydrocarbon fuels, Mil-Spec RP-1, n-dodecane (as a high-purity simulant for RP-1), methane, and propane, and three copper chamber materials, OFHC, NASA-Z, (3% Ag, 0.5% Zr), and ZrCu (0.15% Zr).

The apparatus incorporates two fuel delivery subsystems, one for high-pressure methane, the other for RP-1, n-dodecane, and propane. The RP-1 and n-dodecane were tested at ambient temperature inlet conditions. The methane and propane were subcooled to between −129 and −73°C (−200 to −100°F) enroute to the heated copper test specimen. The test specimen was heated within the carbothermal materials tester without the use of direct ohmic heating. The apparatus incorporates appropriate filters, thermocouples, pressure transducers, propellant thermal conditioners, and mass flowmeters to control and measure the test conditions and record the test data on-line. A port is incorporated to provide on-line fuel samples for chemical analysis.

Figure 2 presents a conceptual diagram of the carbothermal materials tester. It utilizes a large copper block that is heated by 10 electrically insulated cartridge heaters embedded in the block. The heat input into the block is transferred by conduction through a test specimen made of the copper material to be tested. The heat is then withdrawn through a 0.020-in.^{2} cooling channel milled in the bottom of each specimen by fuel flowing through the channel. Figure 3 shows photographs of a typical test specimen used in the facility.
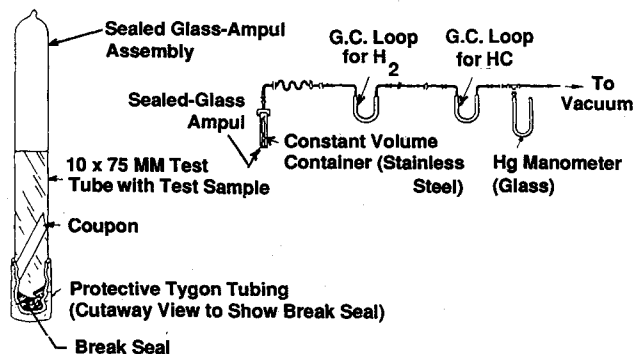
Realistic simulations of cooling channel conditions are produced in this facility without the use of direct ohmic heating of the specimen. Table 1 compares channel conditions produced in the current methane tests with design conditions for the space transportation booster engine (STBE) bipropellant engine. Note that each of the relevant design parameters can be reproduced, including wall temperature, fuel temperature and pressure, fuel velocity, and heat flux through the channel wall.

Another advantage provided by the carbothermal materials tester is that examination of the test specimen can be accomplished directly without disturbing the surfaces that were in contact with the fuel. The RP-1 tests used a simple stainless-steel fuel manifold pressed into the bottom of the test specimen to close out the channel. After the test, separation of the specimen from the manifold exposed the channel. The higher thermal strains encountered in the methane and propane tests required that the channel be closed out with a thin sheet (0.05

Table 1 Typical methane test conditions

	Test conditions	STBE design
Maximum wall temperature, °C	400–500	427
Maximum coolant-side q/A, W/cm^2	8500	8400
Coolant pressure, MPa	29.0	30.8
Coolant velocity, m/s	30–300	90–150
Bulk temperature, °C	−100–190	−129–20
Test duration, s	1000–1800	160/Mission
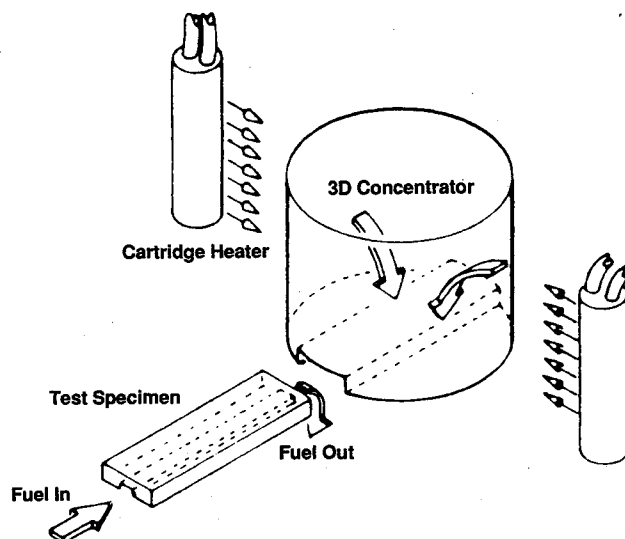
The Geometric Concentration of Energy is an Alternative to Ohmically Heated Test Specimens

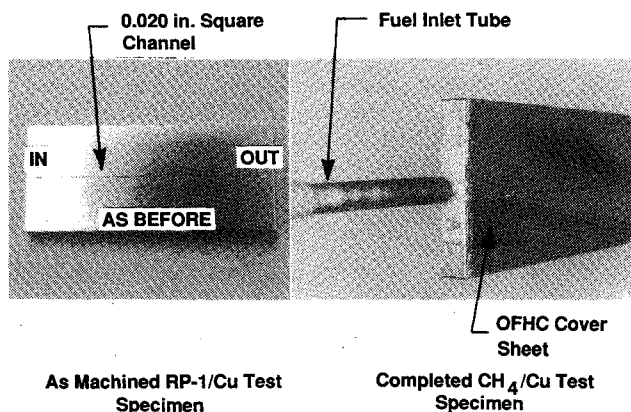Fig. 2 Carbothermal materials tester schematic.

Fig. 1 Sealed glass ampule test schematic.

Fig. 3 Copper test specimen details.

Table 2 RP-1/n-dodecane static test summary

Test no.	Fuel	Impurities	Coupon material	Coupon grain	Coupon strain history	Coupon weight change	Visible coupon change	SEM coupon change	Fuel change
1	RP-1	Air	None						None
2	n-Dodecane	Air	None						None
3	RP-1	Air	316SS	Fine	None	0.0000	None	None	None
4	RP-1	Air	OFHC	Fine	None	0.0000	None	Small	None
5	RP-1	None	OFHC	Fine	None	0.0000	None	None	None
6	RP-1	Air	NASA-Z	Fine	None	0.0000	None	Small	None
7	n-Dodecane	Air + 525 ppm S[a]	NASA-Z	Fine	None	0.0003	Some	Large	Sulfur depletion
8	n-Dodecane	Air + 525 ppm S[a]	OFHC	Large	None	0.0003	Some	Large	Sulfur depletion
9	n-Dodecane	Air + 525 ppm S[a]	OFHC	Large	2% × 40	0.0002	Some	Large	Sulfur depletion

[a]As n-dodecanethiol.

Table 3 Methane static test summary

Test no.	Starting fuel composition	Maximum test pressure, MPa	Maximum test temperature, °C	Coupon weight change, g	Visible coupon change	SEM coupon change	G.C. fuel change
101	UHP Methane[a]	21.2	354	N/A	——	——	None
102	UHP Methane	21.1	349	0.0001[b]	None	None	None
103	UHP Methane + 1% Air	16.4	347	0.0000	Slight tarnish	Small	Oxygen depletion
104	UHP Methane + 2% Ethylene	21.3	342	0.0002	None	None	None
105	UHP Methane	33.2	347	0.0001	None	None	None
106	UHP Methane + Methyl Mercaptan	20.3	347	0.0018	Gray deposit	Heavy deposit	None

[a]Ultrahigh purity methane analysis: methane, 99.5%; sulfur, N.D. (<0.5 ppm); water, <1 ppm; oxygen, 6.0 ppm; and nitrogen, 41 ppm.
[b]All tests used NASA-Z coupons.

cm) of OFHC copper welded around the channel. After testing, a simple end mill operation opened the channel for examination without disturbing the specimen channel that had been exposed to the flowing fuel.

Analytical Test Methods

Methods employed to look for evidence of reaction between the copper specimens and the hydrocarbon fuels included visual examination of each test specimen, 35-mm photographs of each specimen, scanning electron microscopy (SEM) on many of the specimens, and energy dispersive x-ray (EDX) analysis to determine elemental composition of the surface. Electron spectroscopy for chemical analysis (ESCA) was employed on selected specimens for chemical analysis of surface deposits.

Fuels were analyzed by gas chromatography (GC) and atomic adsorption (AA) before and after exposure to the test specimens. Filters placed upstream and downstream of the test block were analyzed to provide data about possible performance degradation as a result of exposure to the fuel.

III. Test Results

Static Tests

RP-1 and n-Dodecane

A summary of the static test results obtained with Mil-Spec RP-1 and n-dodecane (>99% wt% $C_{12}H_{26}$, <1 wt% $C_{11}H_{24}$) with OFHC and NASA-Z copper specimen is presented in Table 2. The test conditions were the same in all of these tests, i.e., the glass ampules were maintained at 204±3°C (400 ±5°F) for 14 days. Test nos. 1 and 2 served as the control tests for RP-1 and n-dodecane, respectively. The sulfur impurity in test nos. 8, 9, and 10 was in the form of n-dodecanethiol. A cursory look at the potential effects of copper grain size and strain history was made in test nos. 9 and 10. The copper specimens were in the form of small rectangular coupons (ca. 2.5 cm × 0.6 cm × 0.05 cm).

No discernible reaction occurred in the copper specimen test in which dissolved air was removed from the fuel before sealing the glass ampule, i.e., test no. 5. The SEM analysis of the copper specimen in which dissolved air was present indicated a small change in the specimen surface, i.e., test nos. 4, 6, and 7.

The change was attributed to the formation of copper oxide. The copper specimens in the tests in which sulfur was added to the fuel were severely tarnished. The change was attributed to the formation of copper sulfide. Analysis of the fuel used in these tests indicated that the n-dodecanethiol was partially consumed. The specimen from test nos. 8, 9, and 10 appeared to be precisely the same, indicating that grain size and strain history did not have a primary effect on the reaction between the copper and the n-dodecanethiol. The body of evidence from the fuel analysis indicated that the RP-1 and n-dodecane did not react under these test conditions.

Methane

A summary of the static test results obtained with ultrahigh purity methane (99.97 vol%) with NASA-Z copper specimens is presented in Table 3. The maximum duration of these tests was 5 h, with specimens at the maximum test temperature for approximately 0.5 h. Test no. 101 served as the control test. Air and ethylene were the added impurities in test nos. 103 and 104, respectively. Methyl mercaptan served as the sulfur (272 ppm) impurity in test no. 107. The NASA-Z coupons were in the form of discs (2.5-cm diam × 0.05 cm) in all tests.

Discernible reaction occurred in only two tests, i.e., test nos. 103 (air) and 107 (methyl mercaptan). Only oxygen and sulfur reacted to tarnish/corrode the NASA-Z coupons. Methane and ethylene did not react under the conditions of these tests.

Propane

A summary of the static test results obtained with instrument grade (99.5 vol%) and research grade (99.99 vol%) propane with NASA-Z and ZrCu copper specimens is presented in Table 4. The maximum duration of these tests was 5 h, with the specimen at the maximum test temperature for approximately 0.5 h. Test no. 110 served as the control test. Test no. 106 was conducted with instrument grade propane and resulted in a slight tarnish on the coupon. Subsequent static tests were conducted with research grade propane.

The results of test no. 108 were impacted by the unintentional contamination of the bomb with air. Test nos. 109 and 111 showed the research grade propane and propylene did not

react with the copper test coupons. Test no. 112 investigated the effect of water as a contaminant in the hydrocarbon fuel. A bomb environment was prepared with research grade propane and 2000 ppm water. The heavy tarnish and weight gain developed on both specimens indicate that a high water content in the hydrocarbon fuel can react with the copper alloys.

Test no. 113 showed again that the addition of methyl mercaptan (at 94 ppm) to the hydrocarbon fuel reacted to corrode both the NASA-Z and the ZrCu coupons. Both exhibited a heavy coating of copper sulfide and a relatively large weight gain.

In most of the propane tests, a small amount of ethane (200–300 ppm) was formed, indicating the propane undergoes a small degree of thermal decomposition at the conditions of these tests.

Dynamic Tests

RP-1 and n-Dodecane

A summary of test conditions for Mil-Spec RP-1 and n-dodecane, respectively, is presented in Table 5. Testing with n-dodecane was conducted to simulate "ultrahigh purity" RP-1. The Mil-Spec for RP-1 allows the presence of many chemical compounds, including unsaturated hydrocarbons, compounds containing oxygen and nitrogen, metal deactivators, and even mercaptan and inorganic sulfur compounds. In contrast, the n-dodecane used in this test program was analyzed to contain less than 2 ppm of each of these types of compounds. The testing with these two fuels led to several important observations.

First, a black tar-like deposit was formed on the walls of the copper cooling channels in many of the RP-1 and n-dodecane tests, which adversely affected the heat transfer performance of the cooling channel. The severity of the deposit and the

magnitude of its effect on the heat transfer performance of the specimen was found to be highly dependent on the wall temperature of the cooling channel. Operation at wall temperatures below 304°C (580°F) greatly reduced the amount of deposit formed on the channel walls and essentially eliminated its impact on heat transfer performance. Figure 4 illustrates this point.

Metallographic and chemical analysis of the specimens showed the deposition to be very thin, but tenacious, and chemically very complex. SEM pictures of the surface of a NASA-Z specimen (Fig. 5) show a very uneven, nonhomogeneous layer of tar on the surface of the channel. ESCA analysis of this surface showed the deposit to consist primarily of carbon and oxygen. Bonding information provided by this analysis showed the surface deposit to be in the form of long-chain hydrocarbons, with evidence of ester and ether linkages.

Second, comparison of tests conducted with RP-1 with tests conducted with n-dodecane at similar conditions shows no significant difference in deposition rates or heat transfer performance. Thus, it does not appear than ultrahigh purification of the RP-1 will offer an effective solution to the deposition problem observed at high channel temperatures.

Third, the addition of 50 ppm of sulfur (the allowable limit for mercaptan sulfur in RP-1) substantially changed the interaction of the RP-1 and copper. The copper was actively corroded and was found in the filter and fuel samples taken from this test. SEM pictures of the channel after exposure to RP-1 containing 50 ppm sulfur (Fig. 6) show a definite roughening of the channel surface. At high magnification, these rough areas appear to be "barnacles" of copper sulfide growing out of the channel wall. This appearance is very similar to that reported previously.[2]

Table 4 Propane static test summary

Test no.	Starting fuel composition	Maximum test pressure, MPa	Maximum test temperature, °C	Coupon weight change, g	Visible coupon change	SEM coupon change	G.C. fuel change
106	Instrument propane[a]	24.3	342	0.0001	Slight tarnish[c]	Very slight	None
108	Research propane[b]	26.1	363	0.0001 0.0001	Major discolor	Major oxidation	Depletion of oxygen
109	Research propane	25.3	346	−0.0001 −0.0001	Very slight tarnish	Very slight	Formed ethane
110	Research propane	25.3	351	N/A	N/A	N/A	Formed ethane
111	Research propane + 2% propylene	25.1	346	−0.0001 −0.0001	Very slight tarnish	Very slight	Formed ethane
112	Research propane + 200 ppm water	23.8	348	0.0004 0.0003	Heavy tarnish	Major oxidation	Formed ethane
113	Research propane + methyl mercaptan	24.5	344	0.0014 0.0012	Even coating	Major sulfidation	Formed ethane

[a]Instrument grade propane analysis: propane, 99.5%; sulfur, N.D. (<2 ppm); water, 200 ppm; and oxygen, 6.0 ppm.
[b]Research grade propane analysis: propylene, 55 ppm; oxygen, <5 ppm; ethylene, <1 ppm; sulfur<2 ppm; ethane, 270 ppm; water, 2 ppm; and butane, <5 ppm.
[c]All tests used both NASA-Z and ZrCu coupons except test number 110, which used no coupons.

Table 5 RP-1/n-dodecane dynamic test summary

Test no.	Fuel	Additive	Duration, s	Coolant side T_{wall}, °C	q/A, W/cm^2	Post-test observation
R101	n-Dodecane	None	185	432	2800	Tar-like black deposit
R102	n-Dodecane	None	1624	382	2500	Tar-like black deposit
R103	n-Dodecane	None	3483	388	2000	Tar-like black deposit
R104	n-Dodecane	None	3253	371	2700	Tar-like black deposit
R105	n-Dodecane	None	3118	419	3300	Tar-like black deposit
R106	n-Dodecane	None	2899	426	3100	Tar-like black deposit
R107	RP-1	None	3353	372	2600	Tar-like black deposit
R108	RP-1	None	145	256	2000	N/A
R109	RP-1	None	2853	302	2500	Slight deposit
R110	RP-1	None	257	291	2400	N/A
R111	RP-1	2% 1-Dodecene	2349	202	2800	Slight deposit
R112	RP-1	2% Biphenyl	2519	304	2300	Slight deposit
R113	RP-1	50 ppm Sulfur	2339	308	2400	Corrosion with deposit
			28,337			

Table 6   Methane dynamic test summary

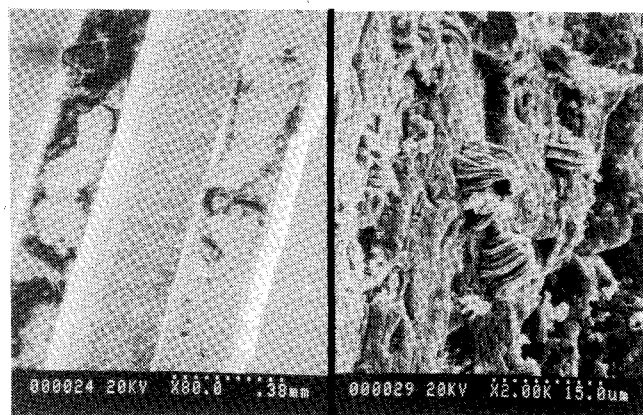| Test no.	Fuel	Additive	Duration, s	T_{wall}, °C	q/A, W/cm^2	Post-test observation
				Coolant side		
101	Methane (tech gr)	None	92	407	4100	Clean walls
102	Methane (tech gr)	None	85	348	3800	Clean walls
103	Methane (tech gr)	None	325	360	4200	Clean walls
104	Methane (tech gr)	None	1069	449	5100	Clean walls
105	Methane (tech gr)	None	1394	492	5300	Clean walls
106	Methane (tech gr)	None	1383	377	4300	Clean walls
107	Methane (tech gr)	None	1200	454	6600	Clean walls
108	Methane (tech gr)	None	819	501	6800	Clean walls
109	Methane (tech gr)	5% Ethylene	1310	404	5100	Clean walls
110	Methane (tech gr)	200 ppm Sulfur	274	462	6700	Channel clogged
111	Methane (tech gr)	10 ppm Sulfur	1798	464	5000	Heavy deposit
112	Methane (tech gr)	None	1414	414	8500	Clean walls
113	Methane (tech gr)	1 ppm Sulfur	1803	384	7300	Thin, even deposit
			13,966			
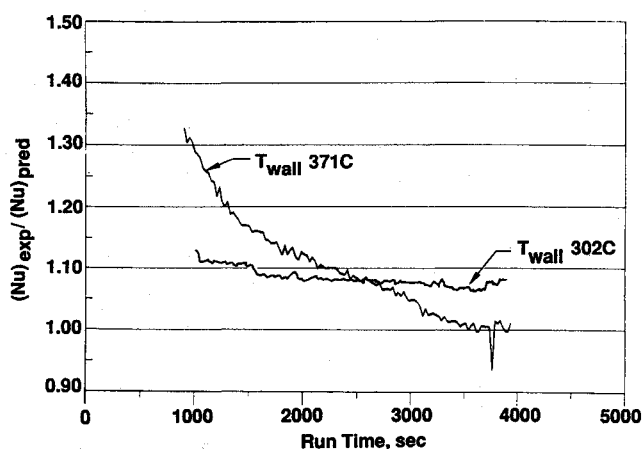
Fig. 4   Heat transfer performance can be affected by RP-1 deposition products.
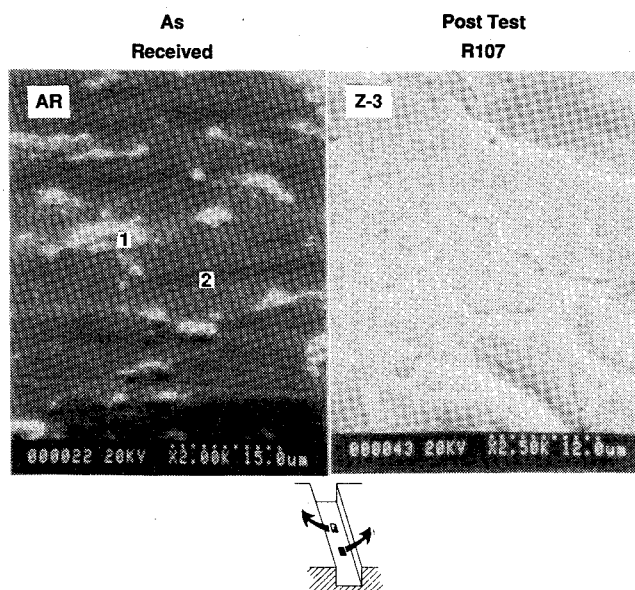
Fig. 5   Photomicrographs show RP-1 deposits after operation at $T_{wall} = 371°C$.

Fig. 6   Photomicrographs show wall roughening after operation with 50 ppm sulfur as n-dodecanethiol.

Methane

A summary of test conditions with methane is presented in Table 6. As noted in the table, all testing was conducted with technical grade methane as the basic fuel. In some tests, the methane was doped systematically with an additive to examine the effect of unsaturated hydrocarbons (test M109), or low levels of sulfur contamination (tests M110, M111, and M113).

Again, several important observations can be drawn from the test results.

First, there was no evidence of significant deposition or corrosion in the channels when technical grade methane was used. Heat transfer and pressure drop measurements through the channel remained steady throughout each run. As well, post-test examination of the channel showed the surface to be unaffected, i.e., microscopic machine marks and smears left by the cutter when the channel was milled were still clearly visible after testing. This result is documented in Fig. 7, which shows SEM photographs of the bottom of a test specimen channel before testing, and a specimen after testing with methane for 830 s at a wall temperature of 501°C (934°F).

Second, severe corrosion of the copper channel resulted when sulfur (in the form of methyl mercaptan) was added to the fuel. Tests were conducted at sulfur concentrations of 200, 10, and 1 ppm (by volume), respectively, in the fuel. In each case, evidence of channel corrosion with the formation of cuprous sulfide, Cu_2S, was found.

In the tests with 200 and 10 ppm sulfur, the buildup of copper sulfide was severe enough to reduce the flow rate through the channel. Figure 8 presents 35-mm photographs taken of the channel after the test conducted with 10 ppm sulfur in the fuel. Note the heavy black deposits on all surfaces in contact with the fuel. SEM examination of this specimen (Fig. 9) documents the dramatic appearance of the channel after exposure to methane plus 10-ppm methyl mercaptan. EDX analysis of these deposits shows them to consist only of copper and sulfur, with no evidence of carbon or oxygen.
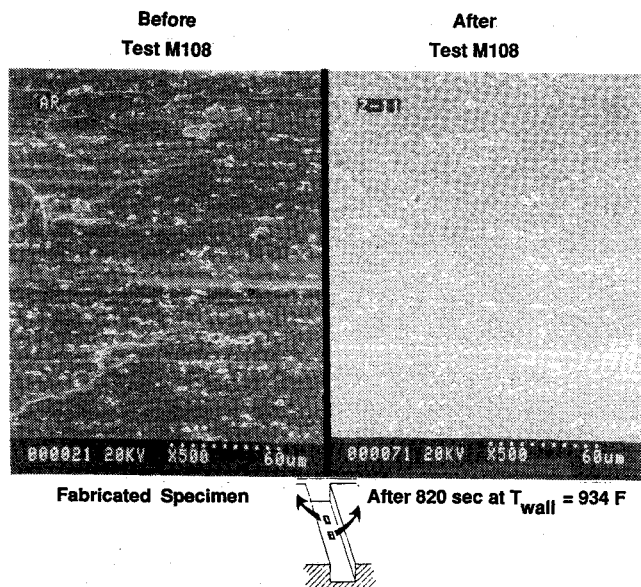
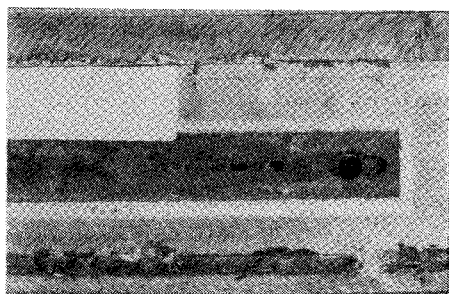Fig. 7   Photomicrographs show channel surface is unaffected after operation with undoped methane.

Fig. 8   35-mm photograph shows clogged cooling channel after operating with 10 ppm sulfur as methyl mercaptan.
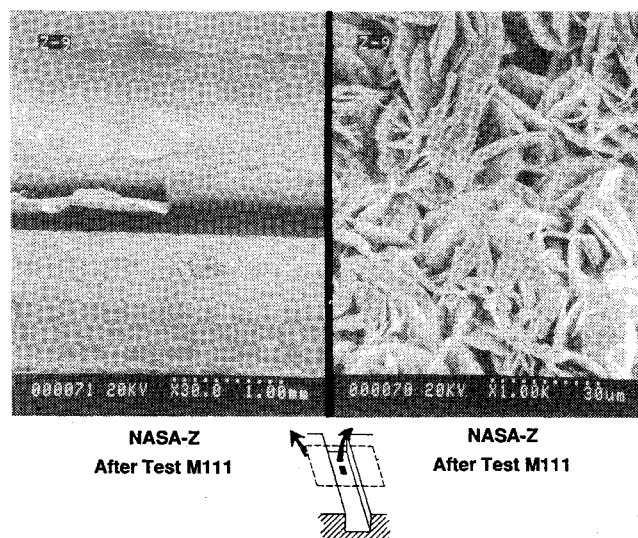

Fig. 9   Photomicrographs show well-defined deposits after operation with methane doped with 10-ppm sulfur as methyl mercaptan.
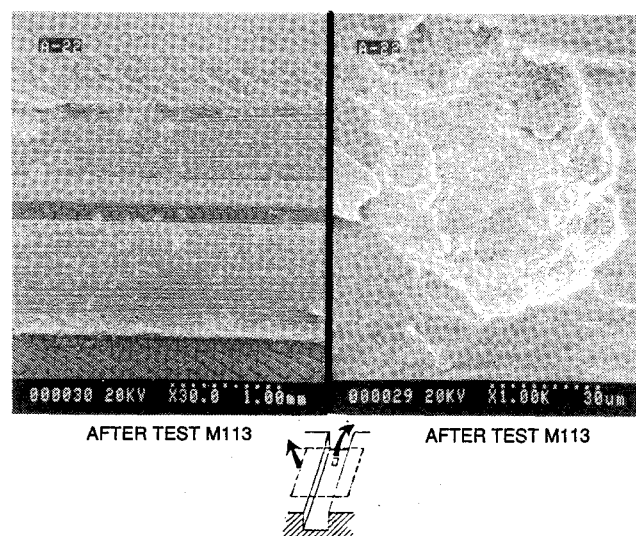

Fig. 10   Photomicrographs show corrosion of channel surface after operation with methane doped with 1-ppm sulfur as methyl mercaptan.

In the test with 1-ppm sulfur, the flow rate was unaffected by the formation of copper sulfide. However, post-test examination of the specimen showed evidence of surface corrosion in the channel. A visible discoloration was left by the 1 ppm of sulfur in the test, which EDX analysis again showed to consist of only copper and sulfur. SEM examination of this specimen (Fig. 10) shows the formation of many "freckles" in the channel which, at high magnification, are actually craters that have formed in the surface. These results appear to be in agreement with those reported in Ref. 3 if one assumes that the fuel was contaminated by trace amounts of a sulfur-containing compound, e.g., hydrogen sulfide.

The mechanism for the corrosion of copper which has been demonstrated in these tests is presented diagrammatically in Fig. 11. It is postulated that when a molecule containing sulfur, such as methyl mercaptan, contacts the copper surface of the channel, the sulfur reacts to form cuprous sulfide. The cuprous sulfide that is created adheres weakly on the surface and can be scoured off by the shearing action of the coolant flowing through the channel, leaving craters in the surface, as evidenced in test M113. On the other hand, if the concentration of sulfur is high enough, the formation of the cuprous sulfide in the channel proceeds faster than the shearing action of the flow can remove it, and massive deposits of cuprous sulfide collect in the channel, as evidenced in the tests conducted with 10- and 200-ppm sulfur in the fuel.

Third, it is interesting to note that the presence of trace amounts of oxygen or water in the methane did not adversely affect the performance of the specimen. The technical grade methane used in this testing contained 4.8 ppm O_2 and 9.0 ppm

water. Post-test surface analysis did not show any evidence of a significant amount of oxygen on the surface of the specimens. These levels of water and oxygen did not impact channel performance.

Propane

A summary of test conditions with propane is presented in Table 7. All testing was conducted with instrument grade propane.

Deposits of cuprous sulfide, Cu_2S, were found in every test specimen exposed to propane. The source of the sulfur is unknown at this time, but is probably due to trace sulfur contamination in the propane, e.g., hydrogen sulfide.

The propane was analyzed by the supplier prior to the conduct of these tests, and no sulfur compounds were found down to a detection limit of 2 ppm. No sulfur compounds were found at a detection limit of 0.2 ppm during subsequent analysis of the gas phase of the propane.

The morphology of the deposits produced during the propane tests was very different from those observed with sulfur-contaminated RP-1 or methane. The deposits formed with

Table 7 Propane dynamic test summary

| Test no.	Fuel	Additive	Duration, s	Coolant side T_{wall}, °C	Coolant side q/A, W/cm^2	Post-test observation
P101	Instrument grade propane	None	2039	338	2000	Powdery black deposit
P102	Instrument grade propane	None	3098	377	4100	Powdery black deposit
P103	Instrument grade propane	None	1394	416	3800	Powdery black deposit
P104	Instrument grade propane	None	3639	430	3500	Powdery black deposit
P105	Instrument grade propane	None	1927	463	3300	Powdery black deposit
P106	Instrument grade propane	None	2229	330	3700	Powdery black deposit
			14,326			
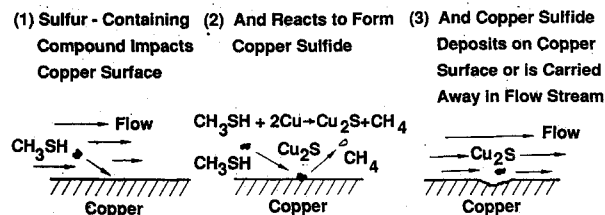
Fig. 11 Postulated mechanism for corrosion of copper by methyl mercaptan.

propane were very powdery and light, with very low adherence to the walls of the channel.

In spite of the sulfur contamination, parametric tests conducted with propane showed that fuel velocity and inlet temperature could impact the test results. At high coolant velocities, i.e., 150–250 ft/s, most of the black deposit was found on the filter downstream of the test specimen. When the coolant velocity was reduced in tests P105 and P106 to 125 and 65 ft/s, respectively, much more of the deposit was found in the channel.

Subcooling the propane reduced the deposition significantly, although it did not eliminate it entirely. Test P105 was conducted with propane entering the channel at ambient temperature, as opposed to the normal starting temperature of − 101 to − 129°C (− 150 to − 200°F). The subcooling reduced the deposition by approximately an order of magnitude.

IV. Conclusions

Tests have demonstrated operation with hydrocarbon fuels and copper chamber materials at conditions representative of those expected in the regeneratively cooled channels of an oxygen/hydrocarbon booster engine. Both reactive and unreactive conditions have been established, and a mechanism for the corrosion of copper by trace sulfur contamination of hydrocarbon fuels has been postulated and demonstrated.

It has been shown that RP-1 can be operated at coolant-side wall temperatures up to 304°C (580°F) without severe coking or corrosion, if the sulfur content of the fuel is controlled.

Methane has been operated at wall temperatures up to 501°C (934°F) without any coking or corrosion, if the sulfur content of the fuel is controlled. Testing has shown that as little as 1 ppm of sulfur (as methyl mercaptan) in the methane corrodes the copper cooling channels.

OFHC, NASA-Z, and ZrCu demonstrate similar behavior. The selection of the copper alloy for chamber design can be made based on other design considerations.

The propane tests have underscored the need to rigorously exclude sulfur from the fuel. Common analytical methods, as were used in the original certification of the propane used in this test series, do not provide adequate assurance of fuel purity. The ultimate utility of propane, uncontaminated by sulfur, as a coolant in copper alloy chamber channel has not been established.

References

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