Reaction 1 control, an increase in pressure from 1 atm (14.7 psia) to 37 atm (543 psia) increases the temperature window with $a_c > 1$ from 427-565°C (800-1050°F) to 427-732°C (800-1350°F). This assumes that temperatures <427°C (800°F) are too low to initiate metal dusting degradation, even though a_c values are high.

4. Calculations also indicate that under equilibrium conditions, all reformer gas mixtures exhibit a_c less than 1 (even at high pressures); therefore, no deposit of carbon and associated metal dusting should occur. Since carbon deposition and metal dusting of structural alloys are widely observed in reformer systems, the gas mixtures in these systems are not really in equilibrium, and a_c is established by individual reactions and is dictated by the reformer effluent gas composition.

5. Calculations further show that experiments need to be conducted under nonequilibrium gas chemistry to deposit carbon (coke) and also allow sufficient incubation time for metal dusting to begin.

6. For Gas Mixtures 4 and 5, a_c will be >1 if Reaction 1 is dominant. If Reaction 2 is dominant, a_c will be >1 at 593°C (1100°F) and <1 at 704°C (1300°F).

Results from these analyses were used to select gas compositions and temperatures for the experimental effort on metal dusting of structural alloys.

EXPERIMENTAL PROGRAM

Equipment Description

In all, five experimental systems were used in the metal dusting experiments. Two existing systems at ANL were modified to accommodate the requirements of the program. Each of the modified systems consisted of a horizontal, tubular, high-temperature furnace capable of operation up to 900°C. The reaction chamber, with gas inlet/outlet fittings, fabricated from quartz was positioned within the furnace chamber. The ends of the reaction chamber had specially designed flanges with O-ring seals. A chromel-alumel thermocouple, inserted from one end of the reaction chamber, was used to monitor the specimen temperature. Specimens were suspended from quartz rods held on the top of a high-purity alumina boat. The specimens and the boat were positioned in the constant-temperature section of the reaction chamber. High-purity gases such as CO, CO_2, CH_4, and H_2 were procured and piped into the reaction chamber through flow meters to obtain the desired composition. In some experiments, H_2 gas was bubbled through a water bath to saturate the H_2 with water prior to entering the reaction chamber. Upon completion of the experiments, the specimens and the carbon accumulated on the specimens and in the boat were removed for detailed microstructural, X-ray, and Raman analysis.

While the two systems described above enabled study of the key variables in metal dusting research, additional facilities were needed for long-term testing of metallic alloys, surface-engineered materials, and coatings. For this purpose, three new systems were designed and assembled in a metal dusting research laboratory. Figure 4 shows a schematic diagram for the three test facilities set up for metal dusting experiments. The three environmental exposure test fixtures are positioned horizontally on a laboratory bench top in a staggered linear arrangement with a common gas supply. Each test fixture consists of a quartz retort chamber (74-cm length, 5-cm OD, 0.32-cm thick), which was centered in a 30-cm-diameter resistive heating furnace. A Barber-Coleman Model 560 three-mode controller is used to control the furnace temperature. The ends of the quartz retort tube are closed by Type 316 stainless steel (SS) flange caps with an O-ring seal. The flange caps provide port fittings for the gas flow, steam/vapor preheater, and ceramic thermowells used for measurements of specimen temperature. Figure 5 shows a schematic diagram for the furnace assembly and gas flow arrangement used for the metal experiments.
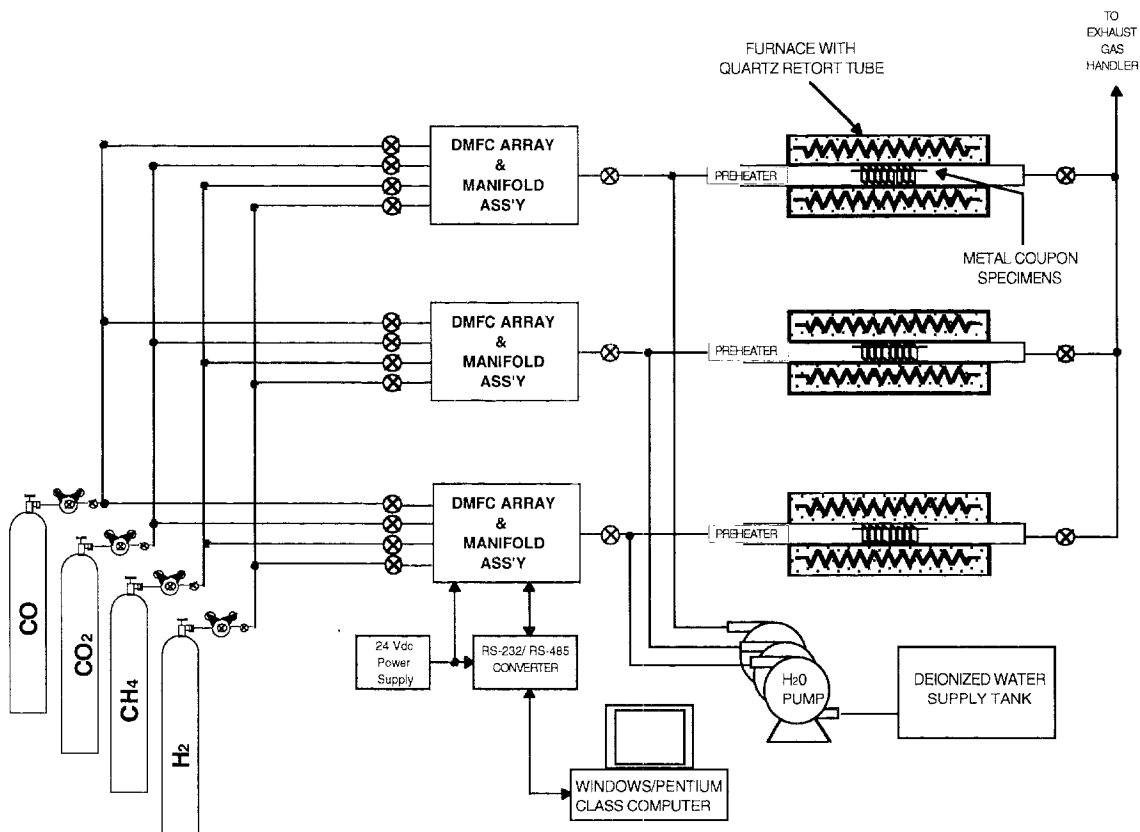

Fig. 4. Schematic diagram for three test facilities set up for metal dusting experiments.
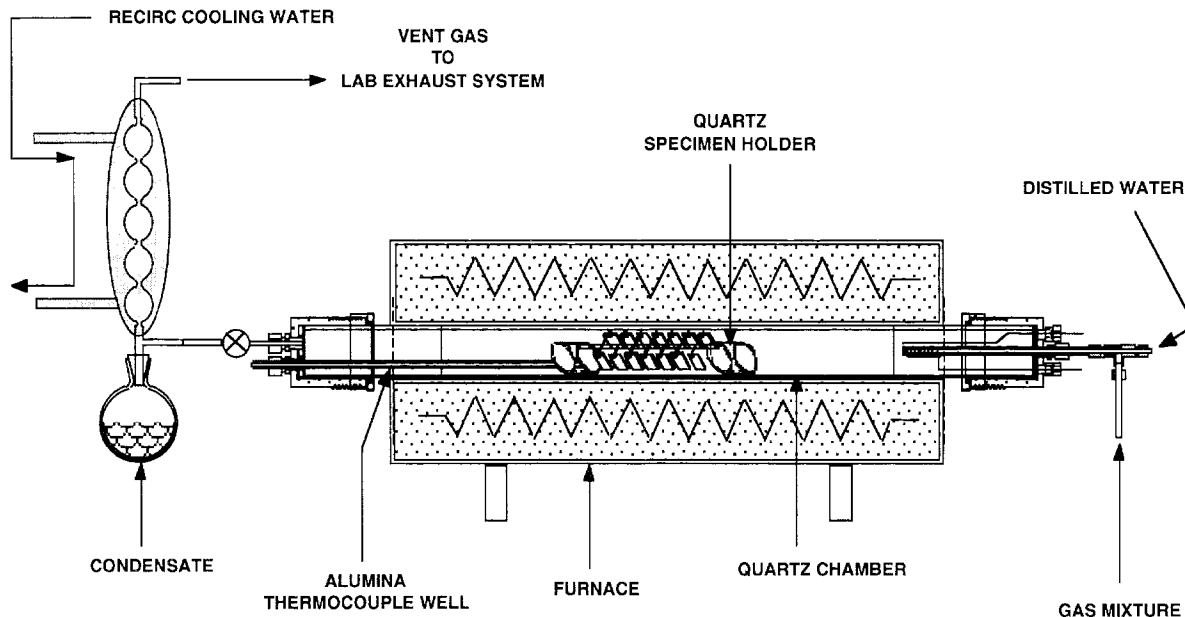
Fig. 5. Schematic diagram of furnace assembly and gas flow arrangement used for metal dusting experiments.

The gas that flows through the retort chamber has various ratios of H_2, CH_4, CO, CO_2, and steam/water vapor. Laboratory-grade compressed gases are supplied from AGA Gas Co. in industry standard 1A size (136 atm and 4.3 m^3 internal volume) cylinders. Each gas is piped to the reaction chamber through a low-pressure manifold line that is fed from a two-stage gas pressure-reducing regulator with a flash arrestor and a solenoid shut-off valve. The solenoid valves are controlled by a gas-leak detection system manufactured by International Sensor Technology Co. Overhead sensors that are selective to H_2, CH_4, CO gases are used to detect gas leaks. In the event of a leak detected above a user-selected threshold by any of the sensed gases, the detection system closes the solenoid valves for all gases.

Gases from the low-pressure manifold lines are supplied to respective individual Brooks model 5850S digital computer-controlled mass flow control (DMFC) valves. Figure 6 shows a schematic diagram of the steam and gas flow scheme used for the metal dusting experiments. The output from each mass flow controller combines into a central manifold tube that connects to the steam/vapor preheater assembly at the input cover flange for the retort tube. The steam/vapor preheater has a coaxial-design mixing chamber enabling the water vapor to be entrained by the flowing gas mixture prior to passing the preheat element. The gas mixture flow rate is typically 200-400 cm^3/min (STP), and the water flow rate is 1-5 cm^3/h. The preheat temperature is maintained with a Love Controls Model 16A three-mode process controller. Distilled water is supplied to the preheat mixing chamber by a Watson-Marlow Model MPL micro-metering pump that is fed from a 20 L poly carbonate carboy.

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Quartz Tube

Stainless Steel Flange Body

Steam Preheat Controller Thermocouple

Gas/H2O Coaxial Mix Line

Distilled H2 O Inlet from Micro-Metering Pump

Steam Preheat Element

O-Ring Seal

Furnace Boundary

Teflon

To Preheat Controller

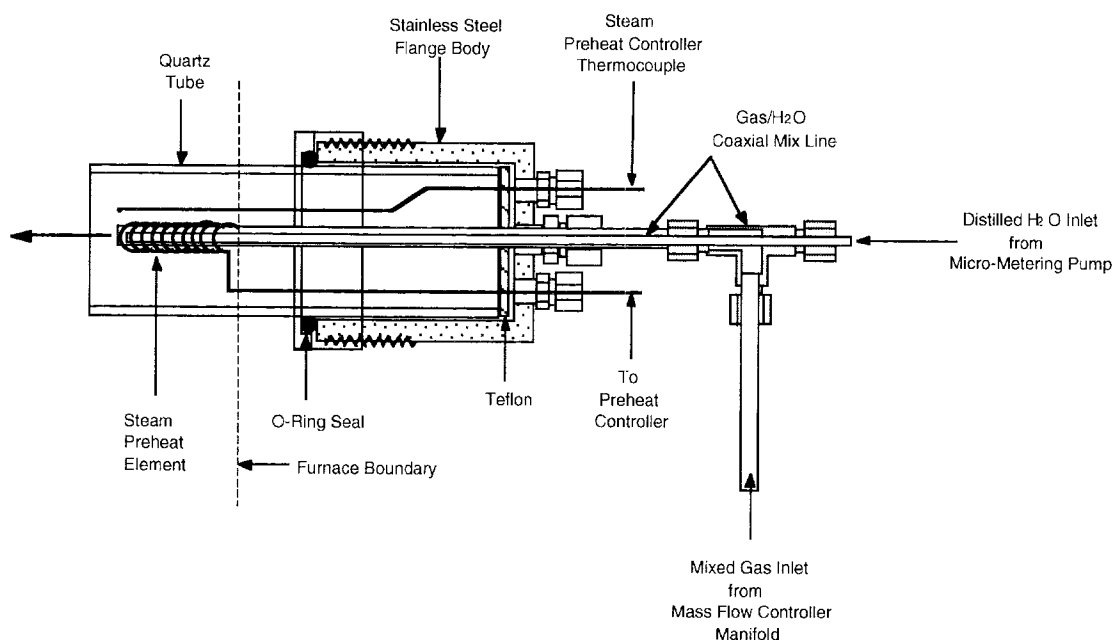Mixed Gas Inlet from Mass Flow Controller Manifold

Fig. 6. Schematic diagram of steam and gas flow scheme used for metal dusting experiments.

The micro-metering pump is based on peristaltic action, and the flow rate is adjusted by varying the rotational speed of the roller cam and/or the diameter of the flexible tubing. The gas-steam mixture flows past the alloy test specimens to the exit port at the rear flange cap. After the gas-steam mixture exits the retort, it is passed through a chilled water pyrex condenser to collect water vapor for future measurement, while the remaining gas mixture is vented to a room exhaust vent handler. Gas composition analysis is available during an exposure test by a Stanford Research Systems Model QMS100 gas analyzer. Each environmental exposure test system has sampling ports at the inlet of the preheat mixing chamber and at the outlet of the chilled water condenser.

Alloy test specimens are mounted on a quartz specimen tree (see Fig. 7) that is centered in the heat zone of the retort chamber. Metal-dusting experiments are conducted under isothermal conditions at temperatures between 800 and 1300°F (427 and 704°C). A chromel-alumel thermocouple controls the furnace temperature. The test temperature and the precision of its control are important to the reproducibility and usefulness of the results. An indicating controller calibrated for the control thermocouple is maintains the furnace temperature. Specimen temperature is monitored with a second, sheathed chromel-alumel thermocouple inserted into the reaction chamber in the vicinity of the specimens. The outputs of the monitoring and control thermocouples are calibrated over the temperature range of interest, so that if the monitoring thermocouple becomes inoperative due to corrosion, the control
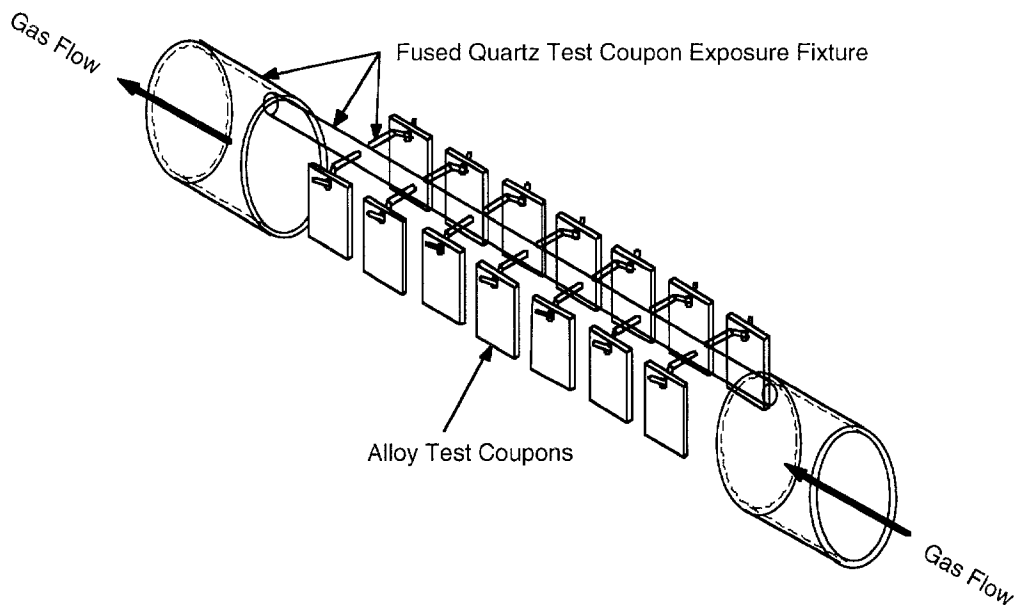
Fig. 7. Schematic diagram of quartz specimen holder and test coupon arrangement used for metal dusting experiments.

thermocouple can be used during continuation of the test. The multicomponent gas environment for the metal dusting program consists of CO, CO_2, H_2, CH_4, and H_2O. The actual composition of the gas mixture has a wide enough range to establish carbon activity of ≈ 0.5 to ≈ 100 at the temperatures and pressures of interest. The exposure time periods in different experiments ranged between 5 and 1000 h, depending on the objective of the test.

Materials

The test program includes a number of Fe- and Ni-base alloys, predominantly those commercially available, selected on the basis of Steering Committee discussions. Heat analysis of all the alloys, supplied by the alloy supplier, is maintained at Argonne National Laboratory. In addition, several surface-engineered alloy specimens (including surface coatings) are being evaluated in the program. Only wrought alloys are currently planned for the test program. Table 3 lists the nominal chemical compositions of the alloys selected for evaluation in the program.

The Fe-base alloys included a low-Cr ferritic steel (T22), an intermediate-Cr ferritic steel (T91), and several high-Cr ferritic and austenitic steels and other alloys. The Cr content of the latter alloys ranged between 17.3 and 26.7 wt.%. The Ni content of the high-Cr alloys ranged between 9.3 and 36.6 wt.%, except for alloys MA 956 and APMT, which contained no nickel. Several of the Fe-base alloys contained a third element such as Al

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Table 3. Nominal chemical compositions (in wt.%) of alloys selected for the
experimental program

Material	C	Cr	Ni	Mn	Si	Mo	Al	Fe	Other
T22	0.20	2.3	–	0.6	0.5	1.0	–	Bal	–
T91	0.08	8.6	0.1	0.5	0.4	1.0	–	Bal	N 0.05, Nb 0.07, V
153MA	0.05	18.4	9.5	0.6	1.4	0.2	–	Bal	N.0.15, Ce 0.04
253MA	0.09	20.9	10.9	0.6	1.6	0.3	–	Bal	N 0.19, Ce 0.04
353MA	0.05	24.4	34.7	1.4	1.3	0.1	–	Bal	N 0.18, V 0.06
321L	0.02	17.4	9.3	1.8	0.5	–	–	Bal	N 0.02, Ti 0.3
310	0.03	25.5	19.5	1.7	0.7	–	–	Bal	–
800	0.08	20.1	31.7	1.0	0.2	0.3	0.4	Bal	Ti 0.31
803	0.08	25.6	36.6	0.9	0.7	0.2	0.5	34.6	Ti 0.6
38815	0.01	13.9	15.3	0.6	5.8	1.0	0.13	Bal	–
MA956	–	20.0	–	–	–	–	4.5	Bal	Ti 0.5, Y_2O_3 0.6
321	0.04	17.3	10.3	1.2	0.4	–	–	Bal	Ti 0.4, N 0.01
APMT	0.04	21.7	–	0.1	0.6	2.8	4.9	Bal	–
4C54	0.17	26.7	0.3	0.7	0.5	–	–	Bal	N 0.19
600	0.04	15.4	Bal	0.2	0.1	–	–	9.7	–
601	0.03	21.9	61.8	0.2	0.2	0.1	1.4	14.5	Ti 0.3, Nb 0.1
690	0.01	27.2	61.4	0.2	0.1	0.1	0.2	10.2	Ti 0.3
617	0.08	21.6	53.6	0.1	0.1	9.5	1.2	0.9	Co 12.5, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	0.2	2.5	Nb 3.7, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	–	2.3	9.3	Ti 0.13, Zr 0.19, Y 0.09
214	0.04	15.9	Bal	0.2	0.1	0.5	3.7	2.5	Zr 0.01, Y 0.006
230	0.11	21.7	60.4	0.5	0.4	1.4	0.3	1.2	W 14, La 0.015
45TM	0.08	27.4	46.4	0.4	2.7	–	–	26.7	RE 0.07
HR 160	0.05	28.0	Bal	0.5	2.8	0.1	0.2	4.0	Co 30.0

or Si, which has a high affinity for O. For example, MA956 and APMT contained 4.5 and 4.9 wt.% Al, respectively. Alloys 153MA, 253MA, and 353MA contained Si in a range of 1.3-1.6 wt.%, whereas Alloy 38815 contained 5.8 wt.% Si.

Generally, the Ni-base alloys had a much more complex chemical composition since they contained Cr (in a range of 15.4-28 wt.%) and several other elements, such as Mo (alloys 617 and 625), Al (601, 617, 602CA, and 214), and Si (45TM and HR 160). Further, several alloys contained Nb, W, and Co, which can also influence the oxidation behavior of the alloys and their resistance to metal dusting attack.

Surface engineering of select alloys was conducted to examine the influence of that treatment on their resistance to metal dusting. The pretreatment involved oxidation of the alloys in an air or low-pO_2 environment at elevated temperatures. In addition, metallic coatings (primarily enrichment of Al or Cr in the surface regions of the alloys) were applied by a pack diffusion process on several Fe- and Ni-base alloys. Prior to evaluation under metal dusting conditions, the coatings were oxidized in air at elevated temperatures to develop adherent chromia or alumina scales.

Specimen Preparation

The samples are flat coupons with approximate dimensions of 12 x 20 x 1 to 2 mm. They are sheared slightly oversize, and their edges are milled to remove cut edges and reduce the coupons to final size. A standard surface finish is used for all alloy specimens. The finish involves a final wet grinding with 400-grit SiC paper. The surface-engineered specimens are used in the as-fabricated condition. In the tests to evaluate the effect of surface preparation on metal dusting, specimen surfaces are prepared by electropolishing, mill annealing, shot peening, etc. Stenciling or electric engraving at the corner of the coupons identified all of the specimens.

Prior to testing, specimens are thoroughly degreased in clean acetone, rinsed in water, and dried. The specimen dimensions are measured to ±0.02 mm, and the total exposed surface area, including edges, is calculated. The specimens are weighed to an accuracy of 0.1 mg.

The specimens are hung from a quartz specimen holder and oriented to expose the large surfaces parallel to the gas flow. The specimen holder is loaded into the reaction chamber at room temperature, and the chamber is closed. The specimens are heated to the desired test temperature in a hydrogen environment. Upon the system attaining the desired temperature, hydrogen gas flow is shut off, and the selected gas mixture is flowed past the specimens. After completion of the test, the furnace is shut off, the gas flow switched from the multicomponent gas to H_2 (at a flow rate of 10 cm^3/min), and the specimens are cooled to room temperature. The specimen holder is retrieved from the reaction chamber, and each specimen is stored separately in a plastic box.

Several analytical approaches and techniques are used to evaluate the tested specimens. These include metal weight gain/loss in as-exposed and cleaned conditions, pitting size and density (pits per unit area of surface), pit depth (average depth over significant number of pits), and substrate penetration as determined by metallographic examination. After the specimens are weighed in the as-exposed condition, deposits on the specimens are mechanically removed with a soft brush, and the deposit material is analyzed for metal content, if warranted. The brushed specimens are cleaned ultrasonically to remove residual deposits and then washed in water and dried. Subsequently, the specimens are weighed, and the weight gain/loss is noted.

The cleaned specimens are examined for surface pits by optical microscopy. This allows determination of the number of pits present in different regions of the specimen and the pit density. In addition, the sizes of several pits are measured and averaged to establish an average pit size.

At the end of a given run, several of the cleaned specimens (after weighing and pit measurement) are cut and mounted on the cut faces for metallographic polishing and

examination in the as-polished condition (with chemical etching, if needed) by optical and/or scanning electron microscopy. Pit depth and substrate penetration thickness are measured in several exposed specimens. The remaining good metal is calculated as the difference between the original thickness and the thickness unaffected by substrate penetration after exposure.

TEST RESULTS AND DISCUSSION

Key Variables for Carbon Deposition and Metal Dusting

Ten short-term runs were conducted in the two existing test facilities to evaluate the role of several variables in the carbon deposition process and in the initiation of metal dusting reactions. Table 4 lists the ten runs conducted along with specifics on the experimental conditions and objectives. The first nine runs were conducted to evaluate the effect of key variables such as exposure time, temperature, water content in the exposure gas, and presence/absence of catatytic material during exposure on the metal dusting initiation. The range of parameters in the scoping tests included exposure times of 5-100 h, temperatures of 593°C (1100°F) and 704°C (1300°F), gas mixtures with and without H_2O, and presence/absence of catalyzing agent. The specimens included pure Fe, pure Ni, Type 304 stainless steel (ss), Alloys 800 and 601, and Fe aluminide intermetallic. Runs 2 and 3 were conducted for 100 h at 593°C (1100°F) in Gas 4 and 5, respectively. Gases 4 and 5 had similar composition (see Table 1 for gas compositions), except that Gas 5 had 2 vol.% H_2O in addition to other gases.

The carbon activity values established by the Gases 4 and 5 are listed in Table 2. Since Gas 4 contained no H_2O, the carbon activities of this gas mixture at 593°C (1100°F) are infinity and 4.98, based on Reactions 1 and 2, respectively. The carbon activity values for Gas 5 at 1100°F are 32.3 and 5.04, based on Reactions 1 and 2, respectively.
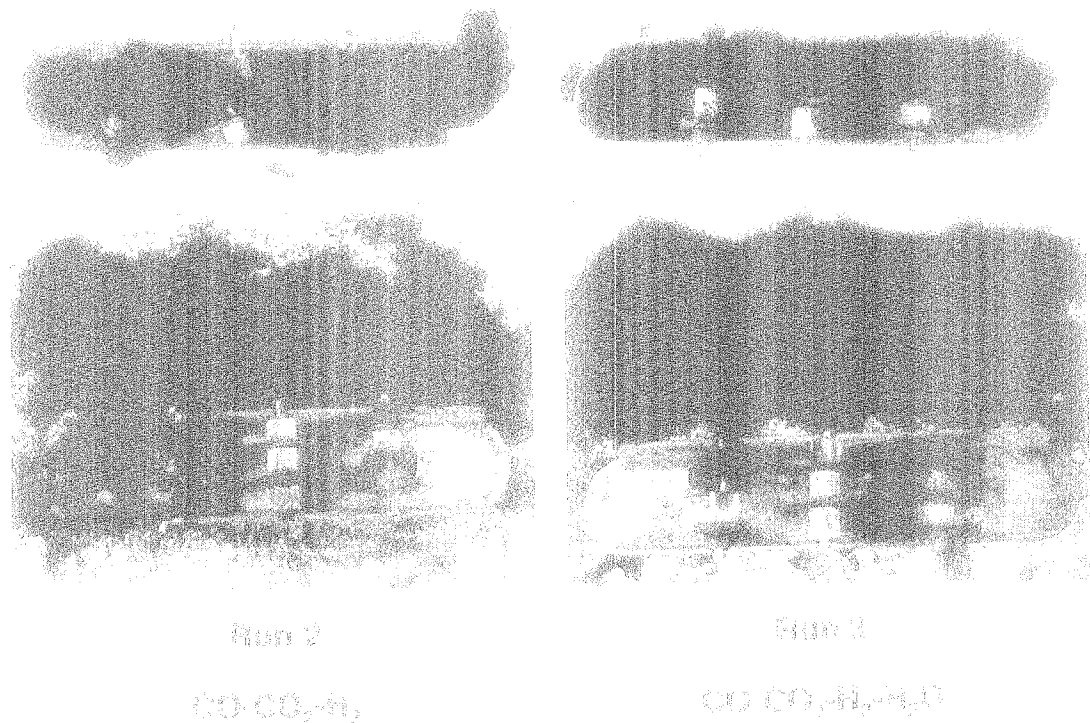
Figure 8 shows macrophotographs of specimens that were exposed in Runs 2 and 3 for 100 h at 593°C (1100°F) in Gas Mixtures 4 and 5. Copious amounts of carbon was deposited on the specimens and on the alumina sample holder. This finding indicates that the gas composition selected for the initial experiments is susceptible to carbon deposition, and addition of 2 vol.% H_2O has very little effect on carbon deposition. In Runs 4 and 5, the specimens were exposed for 100 h in the same gas mixtures but at 704°C (1300°F) instead of 593°C (1100°F). The carbon activities established by Gases 4 and 5 at 704°C (1300°F) are infinity and 3.80 based on Reaction 1, whereas the values are 0.34 based on Reaction 2. The calculations indicate that, if Reaction 1 determined carbon deposition, carbon deposit is expected because $a_c > 1$; on the other hand, if Reaction 2 determined the deposition, no deposit of carbon is anticipated

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Table 4. Experimental conditions for laboratory runs

Run Number	Experimental conditions	Gas mixture	Objective
1	593°C (1100°F), 48 h	Gas 6	Program start
2	593°C (1100°F), 100 h	Gas 4	No water
3	593°C (1100°F), 100 h	Gas 5	2 vol.% H_2O
4	704°C (1300°F), 100 h	Gas 4	Effect of temperature, H_2O
5	704°C (1300°F), 100 h	Gas 5	"
6	593°C (1100°F), 5 h	Gas 5	Effect of time, H_2O
7	593°C (1100°F), 5 h	Gas 4	"
8	593°C (1100°F), 72 h	Gas 4	Ceramics only (no catalysis)
9	593°C (1100°F), 72 h	Gas 5	"
10	593°C (1100°F), 90 h	Gas 4	New system validation
11	593°C (1100°F), 115 h	Gas 4	Fe specimen only
12	593°C (1100°F), 115 h	Gas 4+H_2O	Fe specimen only
13	593°C (1100°F), 100 h	Gas 4+H_2O	Ni specimen only
14	593°C (1100°F), 100 h	Gas 4	Ni specimen only
15	593°C (1100°F), 1000 h	Gas 2	Fe-base alloys
16	593°C (1100°F), 1000 h	Gas 2	Ni-base alloys
17	482°C (900°F), 100 h	Gas 2	Fe specimen only
18	482°C (900°F), 100 h	Gas 2	Ni specimen only
19	593°C (1100°F), 1000 h	Gas 2, low H_2O	Fe-base alloys
20	482°C (900°F), 1000 h	Gas 2	Fe-base alloys
21	482°C (900°F), 1000 h	Gas 2	Ni-base alloys
22	704°C (1300°F), 98 h	High CO Gas	Fe, T91, 304
23	704°C (1300°F), 98 h	"	Ni, Ni-base alloys
24	704°C (1300°F), 102 h	No water	Ni, Ni-base alloys
25*	593°C (1100°F), 1000 h	Gas 2	Fe-base alloys, preox. at 750°C in air
26*	593°C (1100°F), 1000 h	Gas 2	Ni-base alloys, preox. at 750°C in air
27	593°C (1100°F), 142 h	Gas 2	Pack diffusion coatings/Fe-base alloys

*In progress.

because a_C <1. Figure 9 shows the macrophotographs of specimens that were exposed in Runs 4 and 5 for 100 h at 704°C (1300°F) in Gas Mixtures 4 and 5. The occurrence of a significant carbon deposit in these runs indicates that Reaction 1 determines the carbon activity in the exposure environment.

Run 2

$CO-CO_2-H_2$

Run 3

$CO-CO_2-H_2-H_2O$

100 h at 1100°F

Fig. 7 — Macrophotograph of specimens after 100-h exposure in Runs 2 and 3 conducted at 593°C (1100°F)
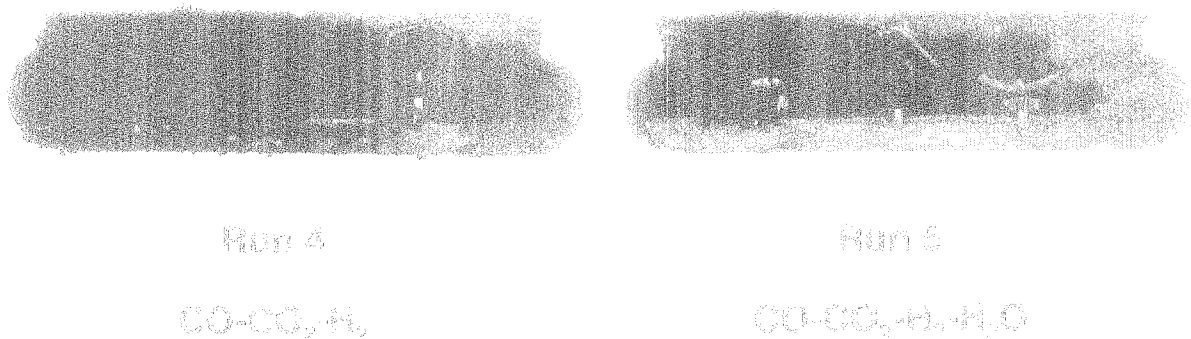

Run 4

$CO-CO_2-H_2$

Run 5

$CO-CO_2-H_2-H_2O$

Fig. 8 — Macrophotograph of specimens after 100-h exposure in Runs 4 and 5 conducted at 704°C (1300°F).

Runs 6 and 7 were conducted to examine the effect of exposure time on diffusion of carbon deposition. Runs were conducted for 10 h at 593°C (1100°F) in Gas Mixtures 4 and 5. Figure 10 shows the macrophotographs of specimens after the 10-h exposure. It is evident that the gas phase reactions accelerated by the catalytic effect of the