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**EFFECTS OF METHANE CONCENTRATION
ON THE CONTROLLED-IMPURITY
HELIUM CORROSION BEHAVIOR
OF SELECTED HTGR STRUCTURAL MATERIALS**

by

W. R. JOHNSON and L. D. THOMPSON

**Prepared under
Contract DE-AT03-76ET35300
for the San Francisco Operations Office
Department of Energy**

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ABSTRACT

The corrosion behavior of candidate structural alloys in a series of three simulated advanced gas-cooled reactor environments at 900°C (1652°F), with methane concentration varied, is discussed. The alloys investigated include three wrought alloys, Hastelloy X, Inconel 617, and Incoloy 800H; two cast superalloys, Rene 100 and IN 713; one centrifugally cast alloy, HK 40; and an oxide-dispersion-strengthened alloy, MA 754.

Corrosion behavior was found to be strongly dependent upon both the alloy chemistry and the environment. Oxidation, carburization, and/or mixed behavior was observed depending upon the specific conditions.

An equilibrium thermodynamics approach has been used to predict alloy behavior and explain observations relevant to the understanding of gas/metal interactions in reactor helium, which inherently contains small amounts of reactive impurity species. Carburization was identified as the primary corrosion phenomenon of concern, and detailed analyses were performed to determine the susceptibility and control of carburization reactions. The presence of alumina scales, containing small amounts of titanium, was found to be particularly effective in inhibiting carburization. Small variations in methane concentration have been shown to have a dramatic effect upon the oxidation potential and subsequent corrosion behavior of the alloy systems.

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1. INTRODUCTION

Advanced high-temperature gas-cooled reactor (HTGR) design concepts require that many structural component materials operate satisfactorily in a temperature range of 800° to 1000°C (1472° to 1832°F) in the presence of the reactor helium coolant for the design life (30 to 40 years) of the reactor. Although helium is itself inert, there are practical limits to the primary coolant helium purity levels obtainable in an operating HTGR. The unavoidable presence of small quantities of potentially corrosive impurities, such as hydrogen (H_2), water (H_2O), methane (CH_4), carbon monoxide (CO), and carbon dioxide (CO_2), requires that an understanding of the interaction(s) of structural materials with these impurities be obtained and taken into consideration in reactor design.

The potential interaction of HTGR primary coolant impurities with reactor structural materials is of prime concern in reactor design, since degradation of properties may result from gas/metal reactions such as internal oxidation or carburization. For example, surface-sensitive mechanical properties, such as fatigue, are likely to be affected to some degree by oxidation at the coolant/metal interface. Carburization may adversely affect the high-temperature strength, ductility, and fracture toughness of an alloy via the intergranular and intragranular precipitation of metal carbides accompanied by matrix depletion of solid-solution-strengthening elements.

Extensive experimental programs are currently in progress at General Atomic Company (GA) to investigate the corrosion behavior of advanced-HTGR structural materials in simulated reactor helium. Efforts were initiated in 1975 as part of the Gas-Turbine and Advanced-HTGR Materials Screening Test Program, representing an international cooperation between GA, the U.S. Department of Energy (DOE), and the then OECD Dragon Project at Winfrith, U.K.

After termination of the Dragon Project, the cooperative program was continued, coordinated by the High Temperature Metals Program (HTMP) organization located at Wimborne, England, and administered by Kernforschungsanlage (KFA), Jülich, Federal Republic of Germany (FRG). This early experimental program included a coordinated series of tests at GA and at the Central Institute for Industrial Research (CIIR) in Oslo, Norway, and involved the exposure of approximately 27 different alloys at 550° to 1000°C (1022° to 1832°F) in helium nominally containing 500 μ atm H₂, 50 μ atm CO, 50 μ atm CH₄, and 1 to 2 μ atm H₂O. A parametric study of the effects of helium impurity concentrations on the corrosion behavior of selected candidate alloys was initiated at GA in 1976 and was broadened in 1977 to the present cooperative U.S./FRG parametric helium impurity corrosion program with GA and KFA as major participants.

The main objective of the current parametric program is to conduct a systematic study of helium impurity/metal corrosion reactions under a full range of projected thermal gas reactor (TGR) environments in order to:

1. Define active corrosion mechanisms and controlling gas/metal reactions as a function of helium chemistry and temperature for representative coolant compositions.
2. Evaluate the influences of helium impurity concentration and temperature on the kinetics of pertinent carburization reactions.
3. Derive helium impurity concentration limits that will minimize corrosion of representative alloy types used in TGRs.

This cooperative program, an extension of the initial GA program, involves the exposure at GA and KFA of a limited number of representative commercial alloys in a broad range of parametrically varied helium environments at 800° to 1000°C (1472° to 1832°F). The selected alloys will be exposed in 31 different helium environments containing controlled amounts of H₂, CO, CH₄, CO₂, and H₂O.

This report presents the results of the first of a series of parametric helium impurity corrosion tests which were initiated during the original GA program and describes the effects of CH₄ concentration on the impure helium corrosion behavior of selected alloys at 900°C (1652°F).

2. EXPERIMENTAL PROCEDURES

The alloys investigated include Rene 100, IN 713, Hastelloy X, Inconel 617, Incoloy 800H, Inconel MA 754, and HK 40. The chemical compositions of the alloys are given in Table 2-1. The compositions listed are the result of analyses conducted by the International Nickel Company (INCO) Research and Development Laboratories with the exception of some producer-certified values as noted in the table. The concentrations of most heavy elements were determined by X-ray fluorescence analyses, while all carbon analyses of as-received alloys and environmentally exposed samples were performed using the LECO combustion method. Trace element analyses for arsenic, bismuth, lead, and selenium on selected alloys were performed using industry-accepted procedures. The material type, potential application, producer, heat number, as-received form, and as-received heat treatment of each test material are presented in Table 2-2.

All corrosion test specimens were in the form of 6.35-mm (0.25-in.) diameter by 25.4-mm (1.00-in.) long cylinders with a centrally located 3.17-mm (0.125-in.) diameter hole drilled near one end for positioning in the specimen holder.

Specimens of the vacuum-shell-cast alloys, Rene 100 and IN 713, were sliced from 6.35-mm (0.25-in.) diameter by 76.2-mm (3.00-in.) long as-cast bars. These specimens were grit-blasted at the foundry with 90 to 120 mesh alumina and were exposed in this surface condition, which is typical of cast turbine components.

The wrought, oxide-dispersion-strengthened (ODS), and centrifugally cast alloy specimens were machined from bar stock, flat stock, and longitudinally cut blanks, respectively, resulting in a uniform surface finish of 8 to 16 rms.

TABLE 2-1
CHEMICAL COMPOSITIONS OF COMMERCIAL ALLOYS STUDIED IN VARIABLE-CH₄ PARAMETRIC HELIUM IMPURITY CORROSION TESTS

Alloy	GA Code No.	Element (wt %)																				
		C	Ni	Fe	Cr	Mn	Si	Mo	Co	W	Nb	Ta	Al	Ti	Cu	V	Zr	Y	B	P	S	Other
Hastelloy X	086	0.080	45.3 ^(a)	20.9	20.5	0.48	0.49	8.60	2.1	0.5	0.25	<0.10	<0.1	<0.1	0.20	<0.10	<0.10	<0.10	<0.002 ^(b)	0.023 ^(b)	0.005 ^(b)	Ca 0.012, ^(b) Mg 0.026, ^(b) Pb <0.001, ^(b) Ag 0.0008 ^(b)
Inconel 617	091	0.064	53.8 ^(a)	0.12	22.6	0.04	0.12	9.15	12.1	<0.10	<0.10	<0.10	1.05	0.33	<0.05	<0.10	<0.01	<0.10	--	--	0.007 ^(b)	Pb 0.0001, Bi 0.0001, As 0.001, Se 0.0002
Incoloy 800H	401	0.07	33.43	43.60	20.36	0.77	0.39	--	--	--	--	--	0.43	0.46	0.49	--	--	--	--	--	0.004	--
Rene 100	061	0.17	59.6 ^(a)	0.11	9.8	<0.02	<0.05	3.15	16.0	<0.10	<0.10	<0.10	5.40	4.10	<0.05	1.09	0.06	<0.10	0.015 ^(b)	--	0.001 ^(b)	--
IN 713	021	0.13	72.0 ^(a)	0.14	13.6	<0.02	<0.05	4.35	0.18	<0.10	2.12	<0.10	6.00	0.85	<0.05	<0.10	0.07	<0.10	0.009 ^(b)	--	0.002 ^(b)	Pb 0.0001, ^(b) Bi < 0.0003 ^(b)
HK 40	321	0.44	20.5	50.9 ^(a)	25.3	0.41	1.32	<0.10	0.15	<0.1	<0.10	<0.10	<0.1	<0.1	0.05	<0.10	<0.10	<0.10	--	--	--	--
Inconel MA 754	121	0.076	75.4 ^(a)	1.76	21.6	<0.02	<0.10	<0.10	<0.05	<0.10	<0.10	<0.10	0.05	0.39	<0.05	<0.10	<0.01	--	--	--	0.004 ^(b)	Y ₂ O ₃ 0.66, ^(b) O ₂ 0.50 ^(b)

(a) Balance of alloy content obtained by difference.

(b) Values from producer certifications.

TABLE 2-2
TEST MATERIAL PROCESSING HISTORY

Alloy	GA Code	Alloy Type	Potential Application	Producer	Heat No.	As-Received Form	As-Received Heat Treatment
Rene 100	061	Vacuum-shell-cast, γ' -strengthened, Ni-base superalloy	Turbine blades/vanes, primary and secondary ducts, fasteners, IHX ^(a) hardware	Howmet	UA043	As-cast test bars	As-cast
IN 713	021	Vacuum-shell-cast, γ' -strengthened, Ni-base superalloy		Howmet	MH1367	As-cast test bars	As-cast
Hastelloy X	086	Wrought, solid-solution-strengthened, Ni-base alloy	Ducts, casings, IHX tubes and hardware, recuperators	Cabot	5-2831	12.7-mm (0.50-in.) diam., round	Solution anneal, 1177°C (2150°F)
Inconel 617	091	Wrought, solid-solution-strengthened, Ni-base alloy		Huntington	XX00A4VS	12.7-mm (0.50-in.) diam., round	Solution anneal, 1149°C (2100°F)
Incoloy 800H	401	Wrought, Fe-base austenitic alloy		Huntington	HH13-6979	19.1-mm (0.75-in.) diam., round	Solution anneal, 1149°C (2100°F)
HK 40	321	Centrifugally cast, Fe-base austenitic alloy	Primary ducts, IHX and PHX ^(b) hardware	Abex	--	133-mm (5.25-in.) o.d. x 89-mm (3.5-in.) i.d. cast tube	As-cast
Inconel MA 754	121	Mechanically alloyed yttrium-oxide-dispersion-strengthened, Ni-base alloy	Primary ducts, IHX hardware	Huntington	DT0039B2-2	25.4-mm (1.0-in.) x 12.7-mm (0.50-in.), flat	Solution anneal, 1316°C (2400°F)

(a) IHX = intermediate heat exchanger.

(b) PHX = process heat exchanger.

All specimens were X-ray radiographed, visually inspected, and weighed prior to exposure. Cast specimens were dye-penetrant inspected at the foundry. Prior to testing the specimens were ultrasonically cleaned for 10 min in a solvent (35% methylethyl ketone, 10% acetone, 15% toluene, 15% isopropyl alcohol, 5% xylene, and 20% ethyl acetate) and then rinsed in ethyl alcohol.

The specimens were exposed isothermally at 900°C (1652°F) for 1000 and 3000 h with interruptions at 500, 1000, 2000, and 3000 h for weight change measurements. Exposures were conducted in three environments consisting of helium containing constant concentrations of H_2 (500 μ atm), H_2O (<0.5 μ atm), and CO (50 μ atm), with CH_4 at three different levels (0, 10, and 100 μ atm).

A schematic diagram of the once-through controlled-impurity helium supply system which generated each desired helium environment is shown in Fig. 2-1. Bottled high-purity nuclear-grade helium was further purified by passing it through a 5 Å molecular sieve and activated charcoal at liquid nitrogen temperature [-196°C (-321°F)]. Controlled quantities of H_2 , CO, and CH_4 were added by metering research-purity gases into the purified helium stream. Each controlled-impurity helium mixture was then introduced into a high-temperature retort and exhausted to atmosphere. No intentional addition of H_2O was made in the present series of experiments.

An overriding consideration in the design of the test system was the minimization of impurity depletion in the retorts so that gas of known and constant composition would be available to react with all specimens during exposure. Specimens were contained in alumina sample holders and exposed in 70-mm (2.75-in.) i.d. by 910-mm (36-in.) long, single-ended alumina retorts, using an alumina gas inlet tube in order to eliminate reactive metal surfaces other than the specimens themselves. In addition to these precautions, flow rates through each retort were maintained at 1000 cm³/min to further minimize changes in gas composition

Fig. 2-1. Schematic diagram of environment control system for parametric helium impurity corrosion study

from inlet to outlet. The impure helium gas mixtures in the retorts were maintained at positive (1.67 atm) pressure to minimize the possibility of air leaks into the test system. Heating of the retorts was accomplished using three-zone Lindberg horizontal tube furnaces with a 610-mm (24-in.) hot zone. The test zone was 75 mm (3 in.) long and contained three equally spaced monitoring thermocouples along its length. The center thermocouple was used for furnace control. Temperature in the test zone was maintained to within $\pm 5^{\circ}\text{C}$ ($\pm 9^{\circ}\text{F}$).

Test monitoring instrumentation included a Carle Model III H (S series) automatic gas chromatograph for determination of H_2 , CO , CO_2 , and CH_4 partial pressures; an EG&G Model 440 extended-range dew point hydrometer for the determination of H_2O partial pressure; and a modified Thermox zirconia cell oxygen probe for the qualitative determination of O_2 partial pressure. The helium composition in and out of each retort was measured, and H_2 , CO , and CH_4 levels were maintained to within $\pm 10\%$ of nominal.

Exposure of the specimens was interrupted at 500, 1000, 2000, and 3000 h for visual examination and weight change measurements. Specimens for destructive analyses were removed after 1000- and 3000-h exposures. All corrosion specimens removed from testing were cut perpendicular to their longitudinal axis to obtain sections for metallography, bulk carbon analysis, and surface studies.

Metallography of etched and unetched sections was performed to study surface corrosion scales, internal oxidation, carburization, and thermal aging effects. Mean oxidation and carburization depths were both measured by taking the average of eight metallographic measurements around the specimen cross section.

Alloy phases and surface scale composition were identified by scanning electron microscope (SEM) microprobe analysis, including selected area energy-dispersive X-ray (EDX) and wavelength analysis.

3. EXPERIMENTAL RESULTS

Interactions between the alloys and impurities in the controlled-impurity helium environments occurred at all exposure times. These interactions were manifested in the form of surface and internal oxide and carbide formation accompanied by alloy depletion, and near-surface, high-density carbide precipitation (carburization). As the result of these environmental reactions, the alloys exhibited varying degrees of surface discoloration, scale formation, changes in weight, and carbon content.

3.1. WEIGHT CHANGE

The measured weight changes of the alloys as a function of exposure time in the 0, 10, and 100 μatm CH_4 environments are shown in Fig. 3-1. These results were normalized with respect to the individual specimen surface area in each case. Those measurements at 500 and 1000 h represent an average of two specimens, while those at 2000 and 3000 h are for a single specimen (one specimen of each alloy was removed at 1000 h for metallographic examination).

With the exception of HK 40, all alloys displayed positive weight changes which increased with increasing exposure time. In general, for those alloys which showed significant changes in weight, a parabolic corrosion rate was observed.

The weight losses observed for HK 40 after a 2000-h exposure in the 0- and 100- μatm CH_4 environments can be attributed to surface scale spallation. In all cases, positive weight changes resulted from either oxidation or a combination of oxidation and carburization.

Relatively small (less than $\sim 0.6 \text{ mg/cm}^2$ after 3000 h) weight changes (except for alloy HK 40 in 100 μatm CH_4) were exhibited by Rene 100, MA

(a)

(b)

(c)

Fig. 3-1. Weight change as a function of exposure time for alloys exposed at 900°C (1652°F) in controlled-impurity helium containing (a) 0 μatm CH₄, (b) 10 μatm CH₄, and (c) 100 μatm CH₄

754, and HK 40 in the three environments and by Inconel 617 at 100 μatm CH_4 . Intermediate (~ 0.8 to 2 mg/cm^2 after 3000 h) weight gains were exhibited by IN 713, Incoloy 800H, Inconel 617, and Hastelloy X at 0 and 10 μatm CH_4 and by Hastelloy X and Incoloy 800H at 100 μatm CH_4 . Alloy IN 713 exhibited a large weight increase ($\sim 3.5 \text{ mg/cm}^2$ after 3000 h) at 100 μatm CH_4 .

3.2. OXIDATION AND SCALE FORMATION

3.2.1. Scale Composition/Morphology

The surface conditions of the alloys after 1000- and 3000-h exposures in the controlled-impurity helium environments were characterized by single-layer or multilayer surface oxide or carbide/oxide scales, internal oxides, and alloy-depleted regions. Zones of high-density carbide precipitation (carburization) extending from the surface inward were also observed and are discussed in Section 3.4. The types, degrees, and compositions of surface scales and internal oxides formed varied with alloy type, exposure time, and CH_4 concentration. Optical and SEM photomicrographs displaying typical surface and subsurface scales observed for the alloys are shown in Figs. 3-2 through 3-9.

Oxide scales were observed on the surfaces of Rene 100, IN 713, and MA 754 for all three environments after 1000- and 3000-h exposures (Figs. 3-2 through 3-4). The scales observed for Rene 100 and MA 754 were continuous and thin and generally confined to the extreme outer surface of the alloys, while IN 713 exhibited a thicker and more penetrating type of oxide scale.

The general morphological character of the oxide scales found on Rene 100 and IN 713 did not vary appreciably with increasing CH_4 concentration for both exposure times, although the extent of oxidation for both alloys was increased between 1000 and 3000 h, especially for IN 713, in which the depth of oxide penetration increased from ~ 20 to $\sim 50 \mu\text{m}$.

RENE 100 (06160)

10 μm

(a)

IN 713 (02174)

10 μm

(b)

MA 754 (12155)

10 μm

(c)

MICROSTRUCTURES SHOW SURFACE CORROSION PRODUCTS IDENTIFIED BY SEM MICROPROBE ANALYSIS: SURFACE OXIDE SCALE (1) AND INTERNAL OXIDES (2). WHITE LAYER ABOVE SCALES IS ELECTRODEPOSITED NICKEL.

Fig. 3-2. Optical photomicrographs showing surface condition and etched subsurface microstructure of Rene 100 (a), IN 713 (b), and MA 754 (c) after 1000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing 0 μatm CH_4 . The surface condition and microstructures are also typical of the alloys after similar exposures in 10 and 100 μatm CH_4 environments.

IN 713 (021)

(a)

IN 713 (021)

(b)

Fig. 3-3. SEM photomicrograph (a) and oxygen K_{α} X-ray map (b) showing surface condition/oxygen distribution for IN 713 after 3000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing 100 μatm CH_4 . The surface condition is also typical of the alloy after exposure in 0 and 10 μatm CH_4 environments.

RENE 100 (061)

(a)

MA 754 (121)

(b)

Fig. 3-4. SEM photomicrographs showing surface condition of Rene 100 (a) and MA 754 (b) after 3000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing 100 $\mu\text{atm CH}_4$

HK 40 (32166)

10 μm

(a)

INCOLOY 800H (40158)

10 μm

(b)

MICROSTRUCTURE SHOWS SURFACE CORROSION PRODUCTS IDENTIFIED BY SEM MICROPROBE ANALYSIS: SURFACE CARBIDE SCALE (1), SURFACE OXIDE SCALE (2) AND INTERNAL OXIDES (3). WHITE LAYER ABOVE SCALES IS ELECTRODEPOSITED NICKEL.

Fig. 3-5. Optical photomicrographs showing surface condition and etched subsurface microstructures of HK 40 (a) and Incoloy 800H (b) after 1000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing 10 μatm CH_4 . The surface condition and microstructures are also typical of the alloys after similar exposures in 0 and 100 μatm environments.

INCOLOY 800H (401) (a)

INCOLOY 800H (401) (b)

Fig. 3-6. SEM photomicrographs showing surface condition of Incoloy 800H after 3000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing (a) 0 $\mu\text{atm CH}_4$ and (b) 100 $\mu\text{atm CH}_4$. The surface condition of the alloy after exposure in a 10 $\mu\text{atm CH}_4$ environment is similar to (a).

HASTELLOY X (08659)

(a)

10 μm

HASTELLOY X (08663)

(b)

10 μm

MICROSTRUCTURES SHOW SURFACE CORROSION PRODUCTS IDENTIFIED BY SEM MICROPROBE ANALYSIS:
SURFACE CARBIDE SCALE (1) AND SURFACE OXIDE SCALE (2). WHITE LAYER ABOVE SCALES IS
ELECTRODEPOSITED NICKEL.

Fig. 3-7. Optical photomicrographs showing surface condition and etched subsurface microstructure of Hastelloy X after 1000-h exposure in controlled-impurity helium environments at 900°C (1652°F): (a) 0 μatm CH_4 environment, (b) 100 μatm CH_4 environment. The microstructure of the alloy after the same exposure in a 10 μatm CH_4 environment is similar to (a).

HASTELLOY X (086) (a)

HASTELLOY X (086) (b)

Fig. 3-8. SEM photomicrographs showing surface condition of Hastelloy X after 3000-h exposure at 900°C (1652°F) in a controlled-impurity helium environment containing (a) 0 μatm CH_4 and (b) 100 μatm CH_4 . The surface condition of the alloy after exposure in a 10 μatm CH_4 environment was similar to (a).

INCONEL 617 (09150A) 0 μ ATM CH_4
(A) 10MM

INCONEL 617 (09154A) 100 μ ATM CH_4
(B) 10MM

PHOTOMICROGRAPHS SHOW SURFACE CORROSION PRODUCTS IDENTIFIED BY SEM MICROPROBE ANALYSIS: SURFACE OXIDE SCALE (1), SURFACE CARBIDE SCALE (2), AND INTRUDED (INTERNAL) OXIDES (3). WHITE LAYER ABOVE SCALE IS ELECTRODEPOSITED NICKEL.

Fig. 3-9. Optical photomicrographs showing unetched surface condition of Inconel 617 typical of 1000- and 3000-h exposures at 900°C (1652°F) in controlled-impurity helium environments containing (a) 0 μ atm CH_4 and (b) 100 μ atm CH_4 . The surface condition of the alloy after exposure in a 10 μ atm CH_4 environment is similar to (a).

The oxide scales observed for Rene 100 were found to be continuous, adherent, and aluminum rich, and to contain small amounts of chromium and titanium (several percent). The scales did not vary significantly in composition with increased exposure time or CH_4 concentration. The oxide scales formed on IN 713 after 1000 h in all three environments consisted of an outer aluminum-rich oxide containing significant amounts of chromium (10% to 15%) and intruded aluminum-rich oxides containing titanium (several percent), while an additional chromium- and titanium-rich oxide developed in patches at the surface of the alloy with increased exposure time (Fig. 3-3).

Continuous and extremely thin titanium-rich oxide scales were observed for MA 754 after a 1000-h exposure in all three environments, while significantly thicker, double-layered chromium- and titanium-rich oxide scales were observed after 3000 h. In addition, the oxide scale formed in the 100 μatm CH_4 environment after 3000 h contained numerous chromium-rich oxide protrusions (see Fig. 3-4).

Multilayer oxide and carbide scales were observed for HK 40, Hastelloy X, and Incoloy 800H in all three environments for both exposure times (Figs. 3-5 through 3-8). Alloy HK 40 exhibited a relatively thick, discontinuous chromium-rich carbide scale over a thinner, continuous, silicon-rich inner oxide scale after a 1000-h exposure for all three environments (Fig. 3-5). The outer carbide scales also contained small amounts of manganese and iron, while the inner oxides contained chromium and aluminum. After a 3000-h exposure, the outer chromium-rich carbide scale on this alloy was observed to be continuous for the 10 μatm CH_4 environment, but had been replaced by a relatively thick, spalling, chromium-rich outer oxide containing small fragments of the original chromium-rich carbide phase in the other two environments. The inner silicon-rich oxide observed after exposure for 1000-h was still found to be intact after the longer exposure.

Triple-layered scales were observed on the surface of Incoloy 800H after a 1000-h exposure in the three environments (Fig. 3-5). The scale was similar for each environment and was composed of a thin, continuous

chromium- and manganese-rich outer oxide layer; a thicker, fairly continuous chromium-rich carbide middle layer; and a thin, continuous chromium- and manganese-rich inner oxide occasionally containing small patches of silicon- and chromium-rich oxide. The chromium-rich carbide phase observed in the three environments also contained small amounts of iron, manganese, and titanium while titanium, silicon, and aluminum were present in the two chromium- and manganese-rich oxide layers. In addition, fine particulate and stringer-type aluminum-rich internal oxides were observed below the surface scales for specimens exposed in all three environments. The depth of this internal oxidation did not vary appreciably with CH_4 concentration after 1000 h.

After 3000 h of exposure, significant differences in scale morphology and/or composition were observed for Incoloy 800H compared with that exhibited after 1000 h (Fig. 3-6). For the 0 and 10 μatm CH_4 environments, the alloy was found to contain triple-layered scales similar to those observed after 1000 h; however, in both cases the inner oxide scale was found to be chromium- and titanium-rich rather than chromium- and manganese-rich, while the outer oxide and middle carbide layer compositions remained similar to those previously observed. For 100 μatm CH_4 , a thick, continuous multilayer oxide scale was observed consisting of a relatively thin outer chromium- and manganese-rich zone, and a thicker middle chromium-rich zone occasionally containing patches of silicon- and chromium-rich oxide. Only small fragments of the chromium-rich carbide scale previously observed were found in this oxide layer. Aluminum-rich internal oxides were also observed below the surface scales in all three environments. The depths of internal oxidation were greater after 3000 h and appeared to increase with increasing CH_4 concentration for this exposure.

Alloy Hastelloy X exhibited a surface scale consisting of a thin, semicontinuous chromium-rich outer carbide and a thin, continuous chromium- and manganese-rich inner oxide after 1000-h exposure in the three environments (Fig. 3-7). The outer carbide scale in each case was occasionally

covered by a thin, discontinuous chromium- and manganese-rich oxide. The carbide scales also contained small amounts of manganese; the oxide scales contained minor amounts of aluminum and silicon. Fine, particulate aluminum-rich internal oxides were observed immediately below the surface scales. The depth of internal oxidation was similar at all three CH_4 concentrations for this exposure time.

After 3000 h of exposure, the Hastelloy X specimens exhibited a relatively thick oxide surface scale containing a fragmented or discontinuous chromium-rich carbide layer (Fig. 3-8). At 0 and 10 $\mu\text{atm CH}_4$, the oxide scale was rich in chromium and manganese and contained significant amounts of the chromium-rich carbide phase. At 100 $\mu\text{atm CH}_4$, the oxide scale observed consisted of an outer chromium- and manganese-rich layer and an inner chromium-rich oxide layer and contained only a very small amount of the carbide phase observed after 1000 h of exposure. Aluminum-rich internal oxides were also observed for this exposure time. The depth of internal oxidation was greater than that observed after 1000 h and increased slightly with increasing CH_4 concentration.

Unlike the surface scales for other alloys exposed in the three environments, the surface scales observed for Inconel 617 exhibited significant morphology and composition differences with increased CH_4 concentration (Fig. 3-9). After a 1000-h exposure in both the 0 and 10 $\mu\text{atm CH}_4$ environments, a surface scale with a thick, discontinuous outer carbide and a thin, continuous inner oxide was observed along with fine particulate and stringer-type internal oxides. Carbide scales for both environments were chromium-rich and contained molybdenum and manganese, while the inner oxide scales were chromium- and titanium-rich and contained minor amounts of aluminum, manganese, and silicon. Internal oxides observed were aluminum-rich and appeared to a greater depth in the 10 $\mu\text{atm CH}_4$ environment. After 3000 h the morphology and composition of the scales observed for the two environments were similar to those observed after 1000 h, although the thicknesses of the scales and depths of internal oxidation were increased.

At 100 $\mu\text{atm CH}_4$, the surface of Inconel 617 exhibited a thin, continuous aluminum-rich oxide scale and contained no internal oxides. The scale morphology and composition were similar for both 1000- and 3000-h exposures except for some slight thickness increase after the longer exposure.

3.2.2. Oxidation Depth

In general, the extent of surface scale and subsurface oxide formation increased with increased exposure time for all of the alloys. Mean oxidation depths as a function of exposure time are presented in Fig. 3-10 and Table 3-1 for all three environments. As the plots in Fig. 3-10 indicate, the alloys exhibited rates of oxidation that generally decreased with increased exposure time. In this regard, their oxidation behavior is similar to the weight change behavior presented in Fig. 3-1. Alloys IN 713, Incoloy 800H, Hastelloy X, and Inconel 617 (in 0 and 10 $\mu\text{atm CH}_4$ only) exhibited the greatest depths and rates of oxidation, reflecting the significant internal oxide formation observed for these alloys. Lowest values were obtained for those alloys which formed only thin surface scales, including Rene 100 and MA 754 in all three environments, and Inconel 617 in the 100 $\mu\text{atm CH}_4$ environment. Alloy HK 40 exhibited intermediate depths and rates of oxidation in the three environments.

The oxidation depths for some alloys also exhibited variations with CH_4 concentration at constant exposure time. After 3000 h of exposure, for example, IN 713 and Incoloy 800H exhibited oxidation depths which were relatively constant between 0 and 10 $\mu\text{atm CH}_4$ and then increased significantly for the highest CH_4 concentration, while those observed for Inconel 617 were also relatively insensitive to CH_4 concentration up to 10 $\mu\text{atm CH}_4$ but decreased at 100 $\mu\text{atm CH}_4$. The oxidation depths observed for Hastelloy X, Rene 100, MA 754, and HK 40 after 3000 h of exposure were relatively insensitive to CH_4 concentration throughout the range of the tests. Similar trends in oxidation depth versus CH_4 concentration were also observed for the alloys after 1000 h.

Fig. 3-10. Oxidation depth as a function of exposure time for alloys exposed at 900°C (1652°F) in controlled-impurity helium containing (a) $0 \mu\text{atm CH}_4$, (b) $10 \mu\text{atm CH}_4$, and (c) $100 \mu\text{atm CH}_4$

TABLE 3-1
SUMMARY OF OXIDATION AND CARBURIZATION DEPTH MEASUREMENTS FOR ALLOYS EXPOSED IN
VARIABLE-CH₄ PARAMETRIC HELIUM IMPURITY CORROSION TESTS^(a)

Alloy	Mean Oxidation Depth (μm)						Mean Carburization Depth (μm)					
	0 μatm CH ₄		10 μatm CH ₄		100 μatm CH ₄		0 μatm CH ₄		10 μatm CH ₄		100 μatm CH ₄	
	1000 h	3000 h	1000 h	3000 h	1000 h	3000 h	1000 h	3000 h	1000 h	3000 h	1000 h	3000 h
Rene 100	5	10	4	10	6	10	32	45	38	45	29	45
IN 713	18	32	17	29	23	42	140	234	140	263	193	460
MA 754	2	3	1	6	1	6	0	0	0	0	0	0
HK 40	5	10	6	16	5	13	51	54	68	45	95	89
Hastelloy X	12	19	12	14	14	18	124	156	133	127	181	178
Incoloy 800H	26	29	29	35	28	51	616	908	600	829	699	911
Inconel 617	20	25	25	27	1	1	167	291	248	800	0	0

(a) All reaction depths were measured from the outer surface. Oxidation depths include internal oxidation where observed. Carburization depths represent the regions of increased near-surface carbide precipitation.

3.3. CARBURIZATION DEPTH

Carburization, resulting from interaction of the alloys with carbon-bearing impurities in the controlled-impurity helium environments and subsequent inward ingress of carbon, was observed in most of the alloys as a near-surface zone of high-density precipitated carbides. These precipitated carbides were both intragranular and intergranular and were generally found (by EDX analysis) to be chromium-rich for all of the alloys. Examples of carburization observed for two of the alloys are shown in Fig. 3-11. Depths of carburization for each alloy were measured on metallographically prepared specimens using optical microscopy. Mean depths of carburization are presented in Table 3-1 and are plotted as a function of exposure time for each environment in Fig. 3-12. These depth measurements represent the penetration distances for the near-surface zones of high-density precipitated carbides.

Significant carburization was observed for Incoloy 800H, Hastelloy X, and IN 713 in all three environments and for Inconel 617 in 0 and 10 μatm CH_4 . Alloy HK 40 exhibited a shallow ($<100 \mu\text{m}$) near-surface band of Widmanstätten-patterned carbides which has been interpreted as carburization for the purposes of this evaluation. No measurable carburization was observed for MA 754 and Rene 100 in any of the environments. Depths of carburization for Rene 100 were expressed as less than the depth of surface alloy depletion resulting from surface scale formation. For those alloys in which significant carburization was observed, rates of carburization, with only a few exceptions (IN 713 in 100 μatm CH_4 and Inconel 617 in 10 μatm CH_4), decreased with increased exposure time. Alloy Incoloy 800H was carburized to the greatest depth (up to $\sim 900 \mu\text{m}$) in all three environments. The least significant carburization for those alloys where carburization was indicated was observed for Hastelloy X.

3.4. BULK CARBON CONTENT ANALYSES

Bulk carbon analyses provide an insight into the relative severity of the carburization phenomena. Table 3-2 and Fig. 3-13 show the results

Fig. 3-11. Optical photomicrographs showing surface condition and internal microstructure of IN 713 and Inconel 617 after 3000-h exposure in a controlled-impurity helium environment at 900 C (1652 F). The microstructure shows increased carbide precipitation near the surface. The white layer above the scale is electrodeposited nickel.

Fig. 3-12. Carburization depth as a function of exposure time for alloys exposed at 900°C (1652°F) in controlled-impurity helium containing (a) $0 \mu\text{atm}$ CH_4 , (b) $10 \mu\text{atm}$ CH_4 , and (c) $100 \mu\text{atm}$ CH_4

TABLE 3-2

BULK CARBON CONTENT OF SPECIMENS EXPOSED FOR 1000 AND 3000 H AT 900°C (1652°F) IN CONTROLLED-IMPURITY HELIUM ENVIRONMENTS CONTAINING 0, 10, AND 100 $\mu\text{ATM CH}_4$

Alloy	As-Received	Wt % Carbon (% Change from As-Received) ^(a)					
		0 $\mu\text{atm CH}_4$		10 $\mu\text{atm CH}_4$		100 $\mu\text{atm CH}_4$	
		1000 h	3000 h	1000 h	3000 h	1000 h	3000 h
Rene 100	0.17	0.16 (-6)	0.16 (-6)	0.16 (-6)	0.16 (-6)	0.16 (-6)	0.16 (-6)
IN 713	0.13	0.16 (23)	0.18 (38)	0.17 (31)	0.17 (31)	0.19 (46)	0.19 (46)
MA 754	0.076	0.049 (-35)	0.003 (-96)	0.055 (-28)	0.036 (-53)	0.032 (-58)	<0.001 (>99)
HK 40	0.44	0.44 (0)	0.45 (2)	0.45 (2)	0.44 (0)	0.45 (2)	0.44 (0)
Hastelloy X	0.08	0.096 (20)	0.097 (21)	0.10 (25)	0.10 (25)	0.11 (37)	0.10 (25)
Inconel 617	0.064	0.092 (44)	0.094 (47)	0.10 (56)	0.097 (52)	0.071 (11)	0.066 (3)
Incoloy 800H	0.07	0.10 (43)	0.11 (57)	0.11 (57)	0.11 (57)	0.11 (57)	0.094 (34)

(a) Values from single determinations on ~0.4-g samples using LECO method.

Fig. 3-13. Relative change in bulk carbon content as a function of exposure time for alloys exposed at 900°C (1652°F) in controlled-impurity helium environments containing 0, 10, and 100 $\mu\text{atm CH}_4$.

of bulk carbon measurements as a function of exposure time and environment. In Fig. 3-13, the shaded areas represent the ranges of change in carbon concentration for the various alloy systems. All alloys except MA 754, Rene 100, HK 40, and Inconel 617 (in the 100 $\mu\text{atm CH}_4$ environment) experienced moderate increases in carbon content in the three environments. Negligible changes in bulk carbon concentration were observed for Rene 100 and HK 40, while MA 754 exhibited decreases in carbon content for all three environments. The amount of decarburization observed for MA 754 increased with increasing exposure time.

Alloys Hastelloy X, IN 713, and Incoloy 800H exhibited increases in bulk carbon content for both 1000- and 3000-h exposures in all three environments. The bulk carbon contents for all three alloys increased with increasing exposure time at 0 $\mu\text{atm CH}_4$ and remained constant with increasing exposure time at 10 $\mu\text{atm CH}_4$. At 100 $\mu\text{atm CH}_4$, the carbon content of IN 713 increased between 1000 and 3000 h, while values for Hastelloy X and Incoloy 800H decreased.

The carbon content of Inconel 617 after 1000- and 3000-h exposures increased with increasing CH_4 concentration up to 10 $\mu\text{atm CH}_4$, while values at 100 $\mu\text{atm CH}_4$ were nearly the same as the as-received value. Bulk carbon values did not change significantly with exposure time for all three environments.

The smallest changes in bulk carbon level were observed for Rene 100 and HK 40 (and for Inconel 617 at 100 $\mu\text{atm CH}_4$). The measured carbon contents of exposed specimens of these alloys are nearly equivalent (within +3% to +11%) to their as-received values and are probably the same within the sensitivity of the measurement technique. The greatest changes in carbon content relative to the as-received values were observed for Incoloy 800H and Inconel 617 at 0 and 10 $\mu\text{atm CH}_4$ (+43% to +57%), Incoloy 800H at 100 $\mu\text{atm CH}_4$ (+34% to +57%), and MA 754 at all three CH_4 concentrations (up to greater than -99%).

4. DISCUSSION

4.1. THERMODYNAMIC CONSIDERATIONS

Carburization, internal oxidation, and surface oxidation in the simulated reactor helium environments investigated are controlled by alloy chemistry, temperature, and the specific environment encountered. Thermodynamic stabilities and kinetics of formation for the oxides and carbides are directly controlled by these parameters, and variations of the parameters can dramatically change the corrosion characteristics.

The environments studied are composed of two (and possibly three) potentially oxidizing species (H_2O and CO , and possibly CO_2) in addition to two potentially carburizing species (CO and CH_4). As has been shown, even for such small concentrations of these species, extensive corrosion can occur in test times of only a few thousand hours.

As for all chemical reactions, the overall driving forces for gas/metal reactions involved in high-temperature corrosion are the free energy changes. However, chemical thermodynamics only predicts the reaction products obtained when equilibrium is reached. It does not provide information on rates of reaction; this is a matter of mechanisms, of reaction kinetics, and of other rate-determining processes. Furthermore, because high-temperature corrosion involves dynamic systems, it should be recognized that metastable compounds or phases as well as intermediate reaction products may be important.

For the equilibrium of the reaction

the free energy change is given by

$$\Delta G^\circ = -RT \ln \left(\frac{a_C a_D}{a_A a_B} \right),$$

where a_C , a_D , a_A , and a_B are the activities of the various components.

If the oxidation of a metal, Me, is considered, for example,

and unit activity of the reactants other than oxygen is assumed, the free energy change reduces to

$$\Delta G^\circ = RT \ln P_{\text{O}_2}.$$

For a metal to be oxidized, the partial pressure of oxygen in the system must be greater than the dissociation pressure of the oxide in equilibrium with the metal. In atmospheres containing varying quantities of CO, CO₂, H₂, and H₂O (as in the present test series), the oxygen partial pressure may be established by the following reactions:

and

With oxygen retained in the standard state, the oxygen partial pressure, or oxygen potential, is given in terms of $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ or $P_{\text{CO}_2}/P_{\text{CO}}$, respectively. The oxidizing potentials of these mixtures are independent of total pressure.

Similarly, the carbon potential of an environment may be established by the reaction

or

Here the carbon potential is determined by the ratio $P_{\text{CH}_4}/P_{\text{H}_2}^2$, $P_{\text{CO}}^2/P_{\text{CO}_2}$, $(P_{\text{CO}})(P_{\text{H}_2})/P_{\text{H}_2\text{O}}$, or $(P_{\text{CH}_4})(P_{\text{CO}})/(P_{\text{H}_2\text{O}})(P_{\text{H}_2})$. For carbon deposition to occur, the equilibrium carbon activity in the gas phase must be unity or higher. Carburization is thermodynamically feasible when the carbon activity in the environment is higher than the carbon activity in the alloy; if the converse is true, decarburization is expected. It is also possible that environmental conditions may produce simultaneous carburization and oxidation by means of reactions such as

In an alloy, the activities of component metals are less than unity, and for a reaction such as

the free energy change for equilibrium is given by

$$\Delta G^\circ = RT \ln \left(\frac{a_{\text{MeC}}}{a_{\text{Me}} a_{\text{C}}} \right) \quad ,$$

With the activity of the reaction product (precipitated as a new phase) taken as unity, this equation reduces to

$$\Delta G^\circ = RT \ln (a_{\text{Me}} a_{\text{C}})^{-1}$$

This equation may be used to calculate the effect of dilution in an alloy if the activity is known. For both oxide and carbide formation, activity considerations can have a marked effect in thermodynamically marginal compound reactions. (Thermodynamic calculations might predict a tendency toward oxide or carbide formation at unit metal activity but not at the actual activity of a metallic element in an alloy.)

4.2. OXIDATION AND SCALE FORMATION

At high temperatures, and when the supply of the oxidizing gas does not limit the reaction rate, an oxide film or scale may be rapidly formed on a metal. The mode, morphology, and composition of the oxide which develops will depend on alloy composition and structure, impurity gas composition, concentration, pressure, temperature, and time. In such cases the reaction is generally governed by solid-state diffusion of the reacting ions (oxygen and/or metal ions) through the film. As the film grows and thickens, oxygen and metal ion gradients are set up in the metal/oxide, the diffusion path increases, and the reaction rate decreases with time, provided the film or scale remains intact.

Grain boundary and short-circuit diffusion will also contribute to the diffusion through the scale, increasing in relative importance with decreasing temperature, and being dependent on grain size, grain boundary structure, and the presence of other internal defects.

Maximum oxidation resistance involves conditions leading to the formation of dense, thin, continuous, and adherent films. Thicker scales may contain internal cracks, pores, and voids which may greatly affect their protective properties. Such scales may also be prone to spallation due to stresses which build up slowly during scale growth or result from thermal cycling due to oxide/alloy substrate thermal expansion differences.

At very low gas pressures, the oxidation behavior (kinetics, morphology of reaction products, etc.) may be significantly changed. Conditions may exist such that the concentration of the reacting gas is sufficiently low to make the supply of reacting gas molecules a rate-determining factor. At such low pressures the reaction may be determined by the rate of impingement of the reacting species on the surface.

The number of oxide nuclei formed on the surface will decrease with decreasing impurity concentration, and at a critical value continuous films will not be formed. A general characteristic feature will be an increasing tendency toward incomplete surface coverage by oxide as the partial pressure is reduced, a continuous protective film being achieved only when isolated oxide particles or islands impinge by lateral growth.

At such very low oxygen partial pressures (10^{-20} to 10^{-25} atm), only certain metals will be oxidized. Metal ions will more fiercely compete with each other for reaction with oxygen. The actual reaction mechanism will depend on a number of parameters, including the relative oxygen affinities (oxide stabilities) of the various oxidizable alloying elements in the metal and the relative diffusion rates of both oxygen and the metallic ions.

Since no CO_2 or H_2O was deliberately added to the environments in the present tests, the oxygen potential of the test environments could have been dominated by either the $\text{H}_2\text{O}/\text{H}_2$ couple or the CO_2/CO reaction, subject to possible reactions with the other impurity species in the

test gases. No CO_2 or H_2O could be detected with the instrumentation (gas chromatograph and dew point hygrometer) used in the tests, and thus it is only possible to calculate upper bounds for the two oxygen potentials based on minimum detectable limits for the two species ($\leq 1 \mu\text{atm CO}_2$, $\leq 0.5 \mu\text{atm H}_2\text{O}$). The two oxygen potentials, both expressed in terms of equivalent $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$, are presented in Fig. 4-1 with stability values for various metal oxides calculated from published free energy data (Ref. 1) using metal activities relevant to the various alloys. In addition, the equilibrium oxygen potentials which are required for the formation of Cr_2O_3 , one of the major surface oxides observed in the tests, are presented in Table 4-1 for three chromium activity levels, 0.2, 0.5, and 0.7, corresponding to the range of chromium activities expected for the various alloys. For the upper bounds indicated in Fig. 4-1, only oxides including and below MnO in the stability diagram would be stable at 900°C (1652°F) in the three environments, subject to reactions among the gaseous impurity species which might tend to reduce either $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ or $P_{\text{CO}_2}/P_{\text{CO}}$. The oxide stability diagram can also be used as a guide for determining the composition of oxide scales which might be expected to form on an alloy of a given chemistry. For example, at 900°C and an oxygen potential of $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 10^{-3}$, an alloy containing chromium and manganese at activities of 0.4 and 0.01, respectively, might be expected to form chromium- and manganese-rich surface oxides. More easily oxidizable elements such as aluminum and titanium, at low enough concentrations ($\sim 1\%$) to preclude formation of continuous surface films, might be expected to appear in internal oxides, their relative concentration with depth being dependent on the oxygen activity gradient produced in this alloy. At higher aluminum and titanium levels, only continuous aluminum- and titanium-rich surface oxides might be possible, thus eliminating some or all of the chromium and manganese from the scale. Such a loss (or replacement) of chromium and manganese in a surface oxide might also be accomplished by further reducing the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio to a point where the oxides of these species, for their particular activities, are no longer thermodynamically stable.

Fig. 4-1. Oxide stability diagram for test alloys at relevant metal activities showing possible oxidation potentials of test environments based on CO_2/CO and H_2O/H_2 equilibria

TABLE 4-1
CORROSION REACTIONS, CORROSION POTENTIALS, AND CORROSION EFFECTS IN VARIABLE CH₄ PARAMETRIC HELIUM IMPURITY CORROSION TESTS

Pertinent Chemical Reaction	Corrosion Effect(s)	Impurity Ratio (Partial Pressures)	Actual Chemical Potential ^(a) (Carbon Activity or Oxygen Partial Pressure)			Required Chemical Potential					
						Carburization ^(b)			Oxidation ^(c)		
			0 $\mu\text{atm CH}_4$	10 $\mu\text{atm CH}_4$	100 $\mu\text{atm CH}_4$	$a_{\text{Cr}} = 0.2$	$a_{\text{Cr}} = 0.5$	$a_{\text{Cr}} = 0.7$	$a_{\text{Cr}} = 0.2$	$a_{\text{Cr}} = 0.5$	$a_{\text{Cr}} = 0.7$
$\text{CH}_4 \rightleftharpoons \text{C} + \text{H}_2$	Carburization/ decarburization	$P(\text{CH}_4)/P(\text{H}_2)$	≤ 4 (≤ 249)	40 (2490)	400 (24,900)	3.7×10^{-3} (7.2×10^{-4})	1.1×10^{-4} (8.5×10^{-5})	3.0×10^{-5} (3.9×10^{-5})	--	--	--
$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	Carburization/ decarburization	$P(\text{CO})^2/P(\text{CO}_2)$	$\geq 2.5 \times 10^{-3}$ (≥ 0.14)	$\geq 2.5 \times 10^{-3}$ (≥ 0.14)	$\geq 2.5 \times 10^{-3}$ (≥ 0.14)	5557 (2.6)	3.9×10^{-1} (3.0×10^{-1})	1.1×10^{-1} (1.4×10^{-1})	--	--	--
$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	Carburization/ decarburization	$P(\text{CO})^2 P(\text{H}_2)/P(\text{H}_2\text{O})$	$\geq 5 \times 10^{-2}$ ($\geq 1.24 \times 10^{-3}$)	$\geq 5 \times 10^{-2}$ ($\geq 1.24 \times 10^{-3}$)	$\geq 5 \times 10^{-2}$ ($\geq 1.25 \times 10^{-3}$)	9.2 (1.8)	2.7×10^{-1} (2.1×10^{-1})	7.6×10^{-2} (9.6×10^{-2})	--	--	--
$\text{CO} + \text{CH}_4 \rightleftharpoons 2\text{C} + \text{H}_2 + \text{H}_2\text{O}$	Carburization/ decarburization	$P(\text{CO}) P(\text{CH}_4)/P(\text{H}_2) P(\text{H}_2\text{O})$	$\geq 2 \times 10^{-1}$ (≥ 0.56)	$\geq 2 \times 10^0$ (≥ 1.77)	$\geq 2 \times 10^1$ (≥ 5.59)	3.3×10^{-2} (1.3×10^{-3})	3.0×10^{-5} (1.8×10^{-5})	2.3×10^{-6} (3.7×10^{-6})	--	--	--
$\text{CO} \rightleftharpoons \text{C} + \text{O}$	Carburization/ oxidation	$P(\text{CO})$	5×10^{-5} (d)	5×10^{-5} (d)	5×10^{-5} (d)	4.6×10^{-4} (4.6×10^{-4})	3.9×10^{-5} (2.9×10^{-5})	8.5×10^{-6} (1.1×10^{-5})	--	--	--
$\text{CO}_2 \rightleftharpoons \text{CO} + \text{O}$	Oxidation	$P(\text{CO}_2)/P(\text{CO})$	$\leq 2 \times 10^{-2}$ ($\leq 1.3 \times 10^{-19}$)	$\leq 2 \times 10^{-2}$ ($\leq 1.3 \times 10^{-19}$)	$\leq 2 \times 10^{-2}$ ($\leq 1.3 \times 10^{-19}$)	--	--	--	1.8×10^{-4}	9.7×10^{-5}	7.8×10^{-5}
$\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}$	Oxidation	$P(\text{H}_2\text{O})/P(\text{H}_2)$	$\leq 1 \times 10^{-3}$ ($\leq 1.6 \times 10^{-22}$)	$\leq 1 \times 10^{-3}$ ($\leq 1.6 \times 10^{-22}$)	$\leq 1 \times 10^{-3}$ ($\leq 1.6 \times 10^{-22}$)	--	--	--	2.6×10^{-4}	1.4×10^{-4}	1.1×10^{-4}

(a) Assumes detection limits of 1 μatm for CH₄ and CO₂, 0.5 μatm for H₂O.

(b) Cr₂₃C₆ formation, (Cr₇C₃ formation).

(c) Cr₂O₃ formation.

(d) Depends on composition of metal oxide and carbide.

In the present tests, oxides of nickel, iron, and molybdenum were not observed in the surface scales of any of the alloys. This observation is in agreement with thermodynamic predictions based on the upper bound for oxygen potential in the tests. Alloys Hastelloy X and Incoloy 800H formed chromium- and manganese-rich surface oxide scales in all three environments, while HK 40 formed chromium- and silicon-rich oxides, Rene 100 and IN 713 formed aluminum-rich oxides, and MA 754 formed chromium-, titanium-, and/or chromium/titanium-rich oxides. Alloy Inconel 617 formed chromium- and titanium-rich oxides at 0 and 10 $\mu\text{atm CH}_4$ and an aluminum-rich oxide surface scale at 100 $\mu\text{atm CH}_4$. In addition, several alloys formed aluminum-rich internal oxides.

The compositions of the surface and internal oxides observed for the different alloys may be rationalized on the basis of the relative activities of the various alloying elements present, e.g., chromium, manganese, aluminum, titanium, etc., and changes in oxidation potential with CH_4 concentration. Based on published data for nickel-chromium, iron-chromium, and nickel-iron-chromium alloys (Ref. 2), the chromium activities for Hastelloy X, Incoloy 800H, and HK 40 at 900°C (1652°F) are expected to be near 0.7, while those for MA 754, Rene 100, and IN 713 should be significantly lower (~ 0.1 to 0.3). The chromium activity for Inconel 617 would be expected to lie in the range of 0.2 to 0.7, depending on the specific effects of the other major alloying elements (molybdenum and cobalt) on the chromium activity in the alloy.

The inclusion of less noble metals in the surface oxide scales of Inconel 617 (titanium at 0 and 10 $\mu\text{atm CH}_4$, aluminum at 100 $\mu\text{atm CH}_4$) compared with that observed for Incoloy 800H and Hastelloy X suggests that the chromium activity for this alloy is near the lower end of the activity range predicted from the published data.

The driving force or chemical potential for the formation of a particular oxide from an alloy is a function of the activity of the

metallic element in the oxide, the oxygen partial pressure of the environment, and the oxide stability. Therefore, with regard to Cr_2O_3 in the present tests, the driving force for the formation of this oxide at a particular favorable oxygen potential ($P_{\text{H}_2\text{O}}/P_{\text{H}_2}$) would be greatest for those alloys with large chromium activities (Hastelloy X, Incoloy 800H, and HK 40), intermediate for MA 754 and Inconel 617 (~ 0.3 chromium activity), and smallest for Rene 100 and IN 713 (~ 0.1 chromium activity). Further, those alloys with lowest chromium activities would be more susceptible to replacement of chromium in the scale by less noble oxide formers, e.g., aluminum, titanium, and silicon, by virtue of a decrease in oxygen potential.

It is suggested that the compositions of the various surface and internal oxides observed varied in a direct fashion with the activities of the metallic elements in the alloys, especially chromium, and the oxygen potential of the test environments. Indirect evidence based on the observed replacement of less oxidizable species with more oxidizable elements in the surface oxides formed at higher CH_4 concentrations suggests a decreasing oxygen potential with increasing CH_4 level in the present tests. Notable in this regard is the apparent loss of manganese from the inner oxides formed on Hastelloy X and Incoloy 800H and the formation of an aluminum-rich oxide on Inconel 617 at 100 μatm CH_4 . Direct evidence for this change in oxidation potential can be established from the results of continuous qualitative measurements made of the oxygen potential ($P_{\text{H}_2\text{O}}/P_{\text{H}_2}$) of the three test environments using an oxygen probe (Thermox) operated at 735°C (1355°F). Although absolute values for P_{O_2} could not be measured because of the inherent limitations of the Thermox device (high oxygen potential reference gas making cell readings susceptible to errors due to oxygen ion back-diffusion, operation at lower than test temperature, etc.), the results suggest a decrease in oxygen potential of approximately two orders of magnitude when the methane level in this series of tests was increased from 0 to 100 μatm .

One possible explanation for the decrease in oxidation potential may be associated with the reaction between CH_4 and the small amount of H_2O (or CO_2) in the environment. At high CH_4 levels, reaction between H_2O and CH_4 may occur to produce small amounts of CO . This reduction in H_2O would result in a lower oxidation potential based on H_2 and H_2O . At lower CH_4 levels, the reaction between CH_4 and H_2O may be kinetically limited and oxidation potentials might remain relatively high.

4.3. CARBON DEPOSITION/CARBURIZATION/DECARBURIZATION

Based on the bulk carbon content and carburization depth data obtained, it was concluded that all three environments at 900°C (1652°F) were strongly carburizing for Hastelloy X, IN 713, and Incoloy 800H; mildly carburizing for Rene 100 and HK 40; and strongly decarburizing for MA 754. The 0 and 10 μatm CH_4 environments were strongly carburizing for Inconel 617 at 900°C , whereas the 100 μatm CH_4 environment appeared to be noncarburizing for this alloy.

Of particular significance in the current tests was the observation of carburization in some alloys after exposure in a 0 μatm CH_4 environment. This behavior suggests that decomposition of CO is an active carburization mechanism at 900°C in the absence of CH_4 and may also play a significant role in carburization in CH_4 -containing helium environments. Carburization depths for Incoloy 800H, Hastelloy X, Rene 100, and HK 40 were relatively insensitive to the CH_4 concentration of the environments (Fig. 4-2), indicating that CO is the dominant carburizing species for these alloys at this temperature, with CH_4 having only a minor influence. On the other hand, the carburization observed for IN 713 in all three environments and for Inconel 617 in the 0 and 10 μatm CH_4 environments suggests that both CO and CH_4 are active carburizing species for these alloys at 900°C .

The increases in bulk carbon content and the appearance of carburization for Hastelloy X, IN 713, Rene 100, and HK 40 in all three environments and for Inconel 617 in the 0 and 10 μatm CH_4 environments are in

Fig. 4-2. Carburization depth versus CH_4 concentration for alloys exposed for 3000 h at 900°C (1652°F) in controlled-impurity helium environments containing 0, 10, and $100 \mu\text{atm CH}_4$.

general agreement with the carburization behavior observed for these alloys after a 3000-h exposure at 900°C in a controlled-impurity helium environment containing 500 μatm H_2 , 1 to 2 μatm H_2O , 50 μatm CO , and 50 μatm CH_4 (Refs. 3-5). Significant carburization was previously observed for Hastelloy X and IN 713, while only small bulk carbon content increases and depths of carburization were observed for Rene 100 and HK 40.

All three environments in the present tests appear to be decarburizing for MA 754, whereas previous 3000-h results indicate no significant changes in bulk carbon content from 900°C exposure in a 50 μatm CH_4 environment. However, the oxygen potential of the environment in the previous tests may have been significantly higher because of the higher H_2O levels (1 to 2 μatm) employed. Bulk carbon content measurements used to assess the degree of decarburization in the present tests indicate that the 10 μatm CH_4 environment was significantly less decarburizing for MA 754 than the 0 and 100 μatm CH_4 environments. The results for this alloy in the present and previous tests suggest that its corrosion behavior may be much more sensitive to changes in impurity concentrations than that of the other alloys.

The apparent change in the carburization behavior of Inconel 617 between 10 and 100 μatm CH_4 is unexpected, since considerable carburization has been observed for this alloy after a 3000-h exposure at 900°C in helium containing 50 μatm CH_4 (Refs. 3-5). However, attendant with this change in carburization behavior in the present tests was a change in morphology and composition of surface scales found on the alloy, resulting from a change in the oxygen potential with increased CH_4 concentration. It is believed that the aluminum-rich oxide formed on this alloy in the 100 μatm CH_4 environment protected the material from subsequent carburization in a manner previously observed for several nickel-base superalloys (Refs. 3,4). It should be pointed out that the surface scales previously observed on Inconel 617 after a 900°C, 3000-h exposure in a 50 μatm CH_4 environment were very similar to those observed in the present tests at 0 and 10 μatm CH_4 .

The carburization behavior of the alloys and their relative susceptibility to carbon pickup can be related to differences in surface catalysis of the decomposition of carbon-bearing impurities, matrix carbon solubility, carbon diffusivity, and the effect of surface corrosion scales on carbon transport.

For carburization to occur in a metal, a carbon activity gradient must exist within the material to provide a driving force for carbon diffusion. The establishment of such a gradient is dependent both on the deposition of carbon at the surface scale/gas interface and on the dissolution of carbon in the surface matrix. Carbon deposition is dependent on the decomposition of carbon-bearing species in the environment (CO , CH_4) and is related to the catalytic effectiveness of the metal surface. Carbon dissolution is dependent on the solubility of carbon in the alloy. If the solubility of carbon in an alloy is very small, carbon cannot be continually introduced into the matrix unless concurrent processes such as carbide precipitation, which may be very slow, can occur to deplete matrix carbon levels. Once carbon has gone into solution, diffusion processes must occur to take the carbon further into the bulk of the alloy. The presence and nature of surface scales (oxides, carbides) can also have a significant influence, since they can limit both carbon deposition by virtue of their catalytic effects and carbon diffusion by providing an effective barrier to carbon transport (Refs. 6-9).

The gas/metal reactions which are potentially capable of producing carbon deposition and/or carburization in the present tests were presented in Section 4-1 [Eqs. (3) through (7)] and include reactions involving all of the impurity species actually (CH_4 , CO , H_2 , H_2O) or possibly (CO_2) present in the test environments. Equilibrium carbon activities for these reactions have been calculated for the test temperature (900°C) and are presented in Table 4-1 along with calculated values for the respective impurity partial pressure ratios or carbon potentials for the three environments. It should be noted, however, that the values calculated for reactions involving H_2O and CO_2 are based on the detection limits for

these species and therefore represent lower bounds for the carbon activities and carbon potentials indicated. Since the carburization observed in the alloys was manifested as a zone of increased carbide precipitation near the surface and these carbides were found by EDX analysis to be primarily chromium-rich, the carbon potentials required for the formation of Cr_{23}C_6 and Cr_7C_3 for three chromium activities (0.2, 0.5, and 0.7) have also been included in Table 4-1. Cr_{23}C_6 has been identified as the primary carbide resulting from carburization of Hastelloy X at 900°C in a controlled-impurity helium environment containing 50 μatm CH_4 (Ref. 10). Both Cr_{23}C_6 and Cr_7C_3 have been observed in a similar alloy (Incoloy 800) exposed to $\text{CO-H}_2\text{O-H}_2$ mixtures at 800° to 1100°C (1472° to 2012°F) (Ref. 11).

For carbon deposition to occur on a metal surface during exposure at high temperature to a gaseous environment containing carbon-bearing species, the carbon activity in the gas phase must be unity or higher. In the present tests, carbon deposition, or soot, was not observed for any of the alloys exposed in the three environments, although the calculated carbon activities based on CH_4 decomposition for all three environments and for reaction of CO and CH_4 at 10 and 100 μatm CH_4 were significantly greater than unity. The calculated carbon activity for CH_4 decomposition at 100 μatm CH_4 , for example, is 24,900. These observations indicate that these two reactions may be kinetically limited under the low impurity partial pressure conditions of the tests.

Carburization of the alloys in the present tests involved the near-surface precipitation of chromium-rich carbides (presumably Cr_{23}C_6 and/or Cr_7C_3). Carbon activities in equilibrium with Cr_{23}C_6 and Cr_7C_3 , for the range of chromium activities expected for the alloys, have been calculated from free energy data for these compounds (Ref. 1). Carburization is thermodynamically feasible when the carbon activity of the environment is higher than the carbon activity in the alloy; if the converse is true, decarburization is expected. In general, the carbon activities in most carbon-containing alloys at high temperatures are high relative to

the thermodynamic stabilities of many carbides, and for this reason there is a continual driving force for matrix carbide precipitation to occur in such alloys, even during thermal aging in non-carburizing environments. These thermal aging phenomena therefore encourage the natural depletion of carbon in these alloys and provide a means by which carbon may be continually introduced into an alloy from an external carburizing source (environment).

It is clear from the calculated values shown in Table 4-1 that the carbon potentials for reactions (3) and (6) were sufficiently high in all three environments to carburize or form Cr_{23}C_6 and/or Cr_7C_3 in all of the alloys, i.e., for chromium activities in the range 0.2 to 0.7. In general, the potential for carburization via these reactions increases with increasing chromium activity. Carburization via simultaneous carbide and oxide formation from CO [reaction (7)] would be potentially possible only for chromium activities of ~ 0.5 and greater, corresponding to that expected for Hastelloy X, Incoloy 800H, and HK 40. Based on the calculated carbon potentials for reactions (4) and (5) using the detection limits for CO_2 and H_2O , these reactions would not be expected to cause carburization in the three environments. However, the carbon potentials based on reaction (5) for the three environments is very near that required for carbide formation in alloys with a chromium activity of 0.7 (i.e., Hastelloy X, Incoloy 800H, and HK 40), and any slight reduction in H_2O level as the result of reaction with CH_4 (as tentatively offered in a previous section to explain the apparent decrease in oxidation potential with CH_4 content) could increase the carbon potential and make this reaction potentially carburizing for these high chromium activity alloys.

Based on the above discussion, reactions involving CO without CH_4 [reactions (5) and (7)] would be potentially strongly carburizing only for alloys with sufficiently high chromium activities (around 0.7), while reactions involving CO and CH_4 or CH_4 alone would be required for carburization of alloys with much lower chromium activities. These thermodynamic considerations may explain why the high chromium activity alloys

like Hastelloy X, Incoloy 800H, and HK 40 exhibited carburization depths which were independent of CH_4 concentration, while others, notably the lower chromium activity alloys IN 713 and Inconel 617, exhibited carburization behavior which was sensitive to CH_4 concentration.

In general, Incoloy 800H, Inconel 617 (except in the 100- μatm CH_4 environment), IN 713, and Hastelloy X, in that order, exhibited the greatest amount of carburization in the three environments. Alloys Rene 100 and HK 40 in all environments and Inconel 617 in 100 μatm CH_4 exhibited near zero to very small carburization depths and bulk carbon increases, while MA 754 was strongly decarburized in all three environments. The enhanced susceptibility of Incoloy 800H, Inconel 617, IN 713, and Hastelloy X is believed to result primarily from the unprotective nature of the surface scales formed on these alloys during exposure, although alloy to alloy differences in matrix carbon solubility, carbon diffusivity, and surface catalysis may have been contributing factors. Alloys Hastelloy X and Incoloy 800H contain higher proportions of iron than the other alloys (except HK 40) in the test series. Recent data indicate that carbon diffusion in Fe-Ni-Cr alloys at 750° to 950°C (1382° to 1742°F) increases significantly with increasing iron content (Ref. 12). At 950°C, for example, an Fe-Ni-Cr alloy with a composition near that of Incoloy 800H (45% iron) would be expected to have a carbon diffusion coefficient ~ 8 times greater than that for Hastelloy X (21% iron) and ~ 10 times greater than that for IN 713 or Inconel 617 ($\sim 0\%$ iron). Incoloy 800H and Hastelloy X are also expected to have much higher carbon solubilities than IN 713 and Inconel 617 because of their high iron contents, since iron is known to increase carbon solubility significantly in Fe-Ni alloys at elevated temperatures (Ref. 13). For example, the carbon solubility in an Fe-25% Ni alloy at 900°C is ~ 0.6 wt %, whereas the carbon solubility in an Fe-60% Ni alloy is ~ 0.1 wt %. In addition, the lower initial carbon contents of Hastelloy X, Incoloy 800H, and Inconel 617 may give these alloys a larger initial potential for accepting carbon into solution compared with the higher carbon alloys exposed. The driving force for initial carbon solution in the matrix is related to the difference between

the carbon solubility limit and the initial carbon content. Therefore, those alloys with a low initial carbon content may have an additional driving force for carburization.

Although the factors described above may have contributed to the rather poor carburization resistance of Hastelloy X, Inconel 617, Incoloy 800H, and IN 713, it is suggested that the primary factor influencing the carburization behavior of these alloys is the non-protective nature of their surface scales. Alloys Hastelloy X, Incoloy 800H, and Inconel 617 (except in the 100 μ atm CH_4 environment) formed complex chromium-rich oxide/carbide surface scales which do not appear to inhibit carbon ingress.

Thin aluminum-rich surface oxide scales were formed on Rene 100 in all three environments and on Inconel 617 in the 100 μ atm environment. Attendant with the formation of these aluminum-rich oxide scales was an almost complete absence of carburization for Inconel 617, while only minor carburization was observed for Rene 100. These results are not surprising since thin aluminum-rich oxide scales have been previously shown to be protective against carburization for a number of nickel-base superalloys exposed in a similar helium environment containing 50 μ atm CH_4 (Refs. 3,4) and for type 406 stainless steel exposed in carburizing atmospheres containing oxygen (Ref. 14).

Thicker, more penetrating aluminum-rich oxide scales were formed on the surfaces of IN 713. In contrast to the thin oxide formed on Rene 100, which contained primarily aluminum (plus some titanium), the oxide scales observed for IN 713 contained aluminum and significant amounts of chromium. Like Rene 100, IN 713 has a chemical composition (high nickel, no iron, relatively high carbon) which would be expected to yield a relatively low carbon solubility and matrix carbon diffusivity, i.e., inherent carburization resistance compared with that expected for Fe-Ni-Cr alloys. However, the alloy experienced significant carburization compared with Rene 100. The addition of chromium to the oxide formed on IN 713 may account for

the apparent defective nature of the scale, which not only allowed carbon to permeate into the alloy but also permitted oxygen to diffuse inward to form internal oxides.

The surface oxide scales formed on HK 40 contained an inner, continuous silicon-rich oxide which may be at least partially responsible for the carburization resistance of this alloy in the three environments, although a portion of this resistance may have been related to the initially high carbon content (~0.4% carbon) of the alloy, which could have decreased the driving force for carbon absorption. The beneficial effects of silicon on both the carburization and oxidation resistance of cast stainless steels, like HK 40, are well known (Ref. 15).

All three environments in the present tests were strongly decarburizing for the oxide-dispersion-strengthened alloy MA 754, and in this regard, the corrosion behavior of this alloy differs strongly from the behavior of the other alloys exposed in the tests. This behavior is rather surprising since MA 754, excepting its Y_2O_3 dispersoid content, has a base composition somewhat similar to that of IN 713. In order for the decarburization of an alloy to occur, the carbon activity in the alloy must be greater than the carbon activity of the environment. It is possible that the yttria dispersoid in this alloy effectively increased its carbon activity or that the loss of carbon from the alloy was in some way connected with the peculiar oxide growth mechanisms associated with oxide-dispersion-strengthened alloys of this type. Oxidation of alloys which do not contain small-diameter ($<1000 \text{ \AA}$) inert oxide dispersoids occurs primarily by the outward diffusion of cation species and subsequent reaction with oxygen-bearing species at the oxide/atmosphere interface. Oxygen ion diffusion through the oxide scales in such alloy systems is limited. The oxidation of oxide-dispersion-strengthened alloys, on the other hand, is primarily controlled by inward oxygen ion diffusion and reaction with metallic ions at the oxide/matrix interface, the dispersoids normally agglomerating below the oxide and blocking the outward diffusion of cations (Refs. 16-18).

5. CONCLUSIONS

The following conclusions can be drawn based on the results of 900°C exposures in the three controlled-impurity helium environments studied:

1. Surface oxidation, internal oxidation, carburization, and/or decarburization can occur singly or in combination via metal/helium impurity interactions at 900°C (1652°F). The type and extent of each corrosion phenomenon are a function of both alloy composition and helium chemistry.
2. Carburization can occur in the presence of CO alone (without CH₄), and for some alloys CO appears to be the dominant carburizing species.
3. Increases in CH₄ concentration can significantly increase carburization in some alloys by providing an additional source of carbon, or can suppress carburization in other alloys by virtue of its effect on the oxidizing potential of the environment.
4. Surface oxides and/or carbide scales based on chromium or containing significant amounts of chromium, and formed in low-oxidation-potential environments, do not inhibit carburization and internal oxidation, whereas thin continuous surface oxides based on aluminum or silicon appear to be protective against carburization and internal oxidation.

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