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EXPOSURE OF REACTOR STRUCTURAL MATERIALS TO IMPURE
HELIUM AT ELEVATED TEMPERATURES

by

A. F. Weinberg and J. M. Scoffin

March 22, 1962

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ABSTRACT

In the High-temperature Gas-cooled Reactor (HTGR), structural metals will be required to operate at temperatures of 1000° to 1400° F in an impure-helium environment for extended periods of time. Six candidate materials for such applications were subjected to simulated reactor environments for times up to 3000 hr to evaluate the extent of corrosion and the changes in mechanical properties occasioned by such exposures.

Under the experimental exposure conditions (helium containing 200 to 300 ppm CO and 200 to 300 ppm H_2 , or helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H_2 , at temperatures of 1200° or 1400° F), oxidation rather than carburization appears to be the major corrosion process; however, in some cases alternating carburization and decarburization were observed. Measurements of weight gains are described. None of the materials studied exhibited a large change in their mechanical properties after exposures at 1200° F. After exposures at 1400° F, moderate changes in mechanical properties were observed for all materials except Type 321H stainless steel, which exhibited a large decrease in ductility after 1500-hr exposure to the higher impurity concentration. In general, the control specimens were affected as greatly as the specimens exposed to the impure helium environments, under the conditions of these tests.

INTRODUCTION

The High-temperature Gas-cooled Reactor (HTGR) under development at General Atomic is UC_2 - ThC_2 fueled, graphite-moderated, and helium-cooled; it includes a heat exchanger and a secondary steam loop for the production of electrical power. It is evident that in such a system impurities may enter the helium stream from a number of sources, the primary ones being in-leakage from the heat exchanger and outgassing of the graphite in the core. Water vapor entering the core from the heat exchanger will react with the core graphite, forming equal concentrations of CO and H_2 , while lesser amounts of CH_4 and N_2 will be present as a result of the graphite outgassing.

It is in such an environment that a number of metal structural components must operate at temperatures ranging from 1000° to 1400° F for extended periods of time. A number of corrosive chemical reactions between this environment and the structural alloys can be postulated, such reactions being either oxidizing or carburizing in nature, depending upon the relative amounts of each impurity present, the alloy chemistry, and the exposure temperature. Because of the complex chemistry of the alloys of engineering interest, it is not possible to predict which reactions will predominate at any given temperature or impurity level; nor is it possible to predict the nature of the reaction products--whether they will be adherent and protective in nature or will be scaly and spall on thermal cycling, or if they will form uniformly or primarily by intergranular attack. In addition, even if one were able to predict the chemical nature of the reaction, it would still not be possible to predict the effect of the reaction products upon the mechanical properties of the exposed metals. For these reasons, it was decided that an investigation should be conducted in which proposed structural materials would be subjected to simulated reactor environments

and changes in their mechanical properties which would be affected by the exposure would be evaluated.

EXPERIMENTAL PROCEDURES

Materials

Six materials that are being considered for structural applications in the HTGR were chosen for this study. The compositions of the five basic metals, which are representative of austenitic stainless steels, ferritic stainless steels, and nickel base alloys, are listed in Table 1. All materials were received in the form of approximately 0.060-in. -thick sheet. The specimens exposed were in the form of tensile and tensile-impact specimens with 1-in. gauge lengths.

Table 1
COMPOSITION OF AS-RECEIVED MATERIALS
(In wt-%)

Material	Cr	Ni	C	Mn	Si	Fe	Ti	Other
321H SS	17.0	10.3	0.083	1.83	0.87	Bal	0.84	Mo, 0.20
347 SS	17.1	10.8	0.066	1.80	0.64	Bal	----	Mo, 0.27 Nb, 0.49
304 SS	17.3	9.5	0.041	1.52	0.64	Bal	<0.03*	Mo, 0.20
430 SS	14.7	<1.0	0.072	0.24	0.39	Bal	<0.02*	Mo, 0.08 S, 0.015 P, 0.038
Inconel [†]	15.5	76.0	0.04	0.35	0.20	7.0	-----	

* Not detected.

[†] Nominal Inconel composition is listed.

For improved creep-rupture properties at elevated temperatures, Type 321 stainless steel is often heat-treated to the H condition; the material used in this investigation was vacuum-annealed at 2200°F for 1 hr, followed by a rapid quench, to achieve the H condition. The resultant grain size was larger than ASTM 1.

One half (i. e. , 120) of the Inconel specimens were aluminized by the Solar Aircraft Company for the purpose of evaluating the efficiency of an aluminum coating in preventing carburization or oxidation that results from gas-metal reactions. A mixture of an aluminum-4%-iron-alloy powder and a flux was sprayed on the test specimens, and the specimens were fired at 1400° F in an argon atmosphere. The specimens were then cooled, the flux was removed, and the specimens were reheated at 1900° F for 1 hr to promote the diffusion of the aluminum coating into the Inconel.

Exposure Conditions

The experimental conditions selected were as follows:

Exposure temperatures	1200° and 1400° F
Exposure environments	Helium containing 200 to 300 ppm CO and 200 to 300 ppm H ₂ Helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H ₂ *
Exposure time	500, 1500, and 3000 hr

The two environments selected are equivalent, on a partial-pressure basis, to impurity levels of 10 ppm H₂O and 100 ppm H₂O, respectively, present at the reactor coolant pressure of 23 atm. The test environments were generated by mixing water-saturated helium with a purified stream of Bureau of Mines helium and reacting this mixture with reactor-grade graphite at 2200° F. A schematic flow diagram of the system employed is shown in Fig. 1. The gas composition was adjusted and monitored by the use of a Loenco Chromat-O-Flex gas chromatograph.

Duplicate or triplicate metal specimens were exposed under each set of conditions. The specimens rested on racks within the retort to allow free gas flow over all the surfaces. In order to separate the changes in

* Only Type 304 stainless steel specimens were subjected to this higher impurity concentration for 3000 hr.

Fig. 1--Schematic diagram of experimental apparatus

properties resulting from prolonged annealing at the temperatures under consideration from those effects caused by exposure to the impure-gas environment, control specimens were employed. All subsequent changes are referenced to these control specimens. The control specimens were sealed in vacuum and annealed at the same temperatures and for the same times as the test specimens.

Evaluations

The following measurements were performed on both the control and the exposed specimens:

1. Weight changes,
2. Tensile properties,
3. Tensile-impact properties,
4. Carbon content,
5. Microstructural changes,
6. X-ray diffraction identification of reaction products.

The weight changes reported are the averages of four to six specimens of each material exposed (including both tensile and tensile-impact specimens); the mechanical properties reported are the averages of the duplicate or triplicate specimens exposed. Samples for carbon analyses were cut from the ends of tensile-impact specimens which exhibited weight gains close to the average for their group. Carbon content was determined conductimetrically. The variation of carbon content between similarly treated specimens was determined and was found to be related to the weight gain of the specimen. Therefore, samples from specimens exhibiting a weight gain close to the average were considered representative of the average carbon content for their group.

EXPERIMENTAL RESULTS

Weight Changes

Measured weight changes, which are a good measure of the kinetics of reaction, are illustrated graphically in Figs. 2 through 5, and are listed in Tables 2 and 3.

All of the 300-series stainless steel specimens exposed at 1200°F to helium with a low impurity concentration behaved quite similarly; the weight changes followed approximately a parabolic rate law to an exposure time of about 1000 hr; at longer times, the rate of weight gain increased with increasing exposure (see Fig. 2). The Type 430 stainless steel, which showed only slight weight gains at 1200°F for exposure times up to 1500 hr, showed an accelerating rate of attack for longer exposure times. The rate of weight gain for Inconel at 1200°F appeared to be decreasing at the longer exposure times. Aluminized Inconel after 3000-hr exposure at 1200°F had an apparent weight loss, which is related to vaporization of the aluminum coating. The latter point was established by qualitative analysis of a vapor-deposited coating on the quartz tube that contained the control specimens. At the higher impurity concentration and/or higher temperature,

Fig. 2--Weight gain of materials exposed at 1200°F to helium containing 200 to 300 ppm CO and 200 to 300 ppm H₂

Fig. 3--Weight gain of materials exposed at 1400°F to helium containing 200 to 300 ppm CO and 200 to 300 ppm H₂

Fig. 4--Weight gain of materials exposed at 1200°F to helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H₂

Fig. 5--Weight gain of materials exposed at 1400°F to helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H₂

Table 2
WEIGHT GAINS AND MECHANICAL PROPERTIES OF SPECIMENS EXPOSED TO IMPURE HELIUM AT 1200°F

Material	Weight Gain (mg/dm ²)			Ultimate Tensile Stress (psi × 10 ³)				0.2% Offset Yield Stress (psi × 10 ³)				Elongation (%)				Reduction of Area (%)				Tensile Impact (ft-lb)			
	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr
Type 304 SS																							
Control	----	----	----	91.8	91.1	91.1	89.7	42.6	38.8	38.6	37.4	73.5	68.7	69.7	61.5	68.9	61.1	70.2	68.6	>240	>240	~240	239
Low*	5.0	7.5	26.0		92.3	91.0	88.5		39.1	39.5	36.6		73.5	69.0	65.0		64.4	64.8	70.9		237	~240	>240
High†	4.3	11.9	----		91.2	91.9	----		38.5	38.1	----		70.0	67.5	----		65.9	63.3	----		~240	231	---
Type 321H SS																							
Control	----	----	----	89.9	93.5	93.8	92.0	29.4	38.9	42.9	43.6	54.5	51.3	46.0	44.0	65.0	54.3	60.3	55.2	209	191	194	195
Low*	6.6	10.2	20.6		91.2	91.5	91.6		35.4	45.5	43.6		52.0	43.0	41.5		55.5	60.4	63.1		190	204	207
High†	12.8	10.9	----		92.5	93.2	----		38.4	45.0	----		47.0	42.5	----		46.4	51.8	----		194	199	---
Type 347 SS																							
Control	----	----	----	106.0	102.0	103.3	101.6	50.6	50.8	49.0	46.3	55.2	49.7	50.0	39.5	66.9	59.6	62.3	51.2	>240	226	223	221
Low*	4.4	7.5	21.5		102.7	103.3	101.5		50.5	49.3	47.4		47.5	48.0	43.5		56.3	62.2	61.7		235	~240	236
High†	6.2	8.8	----		101.3	102.8	----		50.7	47.8	----		47.3	49.8	----		58.4	61.6	----		227	227	---
Type 430 SS																							
Control	----	----	----	71.6	66.6	67.5	66.0	53.5	36.9	37.9	36.8	30.3	32.3	35.7	31.5	67.7	65.8	74.4	78.4	107	117	126	124
Low*	0.4	0.7	9.2		67.3	68.1	67.0		37.5	38.0	37.2		31.5	33.0	32.0		68.7	72.0	83.9		128	134	132
High†	5.0	7.2	----		65.6	66.8	----		36.5	37.2	----		36.7	33.0	----		71.8	74.4	----		115	123	---
Inconel																							
Control	----	----	----	93.8	94.3	94.4	92.2	39.5	39.4	38.7	37.0	45.7	42.3	40.0	41.0	60.7	57.5	63.2	63.6	223	210	203	200
Low*	7.5	22.3	23.3		95.4	96.0	94.4		39.9	38.8	39.0		44.5	43.5	37.5		54.2	53.4	55.8		215	213	226
High†	19.4	23.9	----		95.3	95.3	----		38.9	38.9	----		40.3	40.0	----		48.3	50.4	----		219	224	---
Aluminized Inconel																							
Control	----	----	----	75.8	76.1	79.9	74.8	25.9	29.5	31.7	28.4	39.0	34.3	34.3	32.5	58.0	49.1	53.3	58.0	160	159	169	159
Low*	0.3	1.7	-2.5		77.2	77.8	76.1		30.6	31.0	28.9		36.0	33.0	36.0		57.5	56.2	57.2		169	171	165
High†	2.4	4.3	----		77.0	77.5	----		29.9	29.7	----		(**)	34.5	----		53.6	49.3	----		161	162	---

* Material exposed to low-impurity-concentration helium (200 to 300 ppm CO and 200 to 300 ppm H₂).

† Material exposed to high-impurity-concentration helium (2000 to 3000 ppm CO and 2000 to 3000 ppm H₂).

** Not determined.

Table 3
WEIGHT GAINS AND MECHANICAL PROPERTIES OF SPECIMENS EXPOSED TO IMPURE HELIUM AT 1400°F

Material	Weight Gain (mg/dm ²)			Ultimate Tensile Stress (psi × 10 ³)			0.2% Offset Yield Stress (psi × 10 ³)			Elongation (%)			Reduction of Area (%)			Tensile Impact (ft-lb)							
	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr	As Rec'd	At 500 Hr	At 1500 Hr	At 3000 Hr
Type 304 SS																							
Control	----	----	----	91.8	89.7	87.2	82.1	42.6	34.3	30.9	32.1	73.5	71.0	64.7	43.0	68.9	70.7	63.4	41.2	>240	>240	>240	(**)
Low*	36.6	45.4	38.5		88.8	90.0	88.8		34.0	34.8	33.2		70.3	70.7	60.0		63.4	63.1	68.8		(**)	~240	>240
High†	40.5	60.8	66.5		90.3	89.4	79.3		34.3	33.8	33.2		66.3	68.0	45.3		57.8	59.8	42.5		~240	234	(**)
Type 321H SS																							
Control	----	----	----	89.9	89.2	87.1	90.6	29.4	33.1	31.9	33.0	54.5	45.7	49.5	36.5	65.0	54.7	49.2	44.7	209	186	196	(**)
Low*	54.6	74.0	73.5		93.3	93.3	91.2		35.7	34.8	33.2		44.3	46.7	43.0		47.1	51.9	55.3		184	181	221
High†	56.0	85.2	----		95.9	80.8	----		37.7	35.8	----		43.5	17.5	----		39.5	17.3	----		188	194	---
Type 347 SS																							
Control	----	----	----	106.0	95.6	95.9	88.8	50.6	40.7	40.2	39.8	55.2	46.7	43.0	42.0	66.9	59.2	41.0	54.3	>240	214	(**)	166
Low*	30.6	36.1	41.2		98.9	98.3	97.0		42.3	41.7	39.2		49.7	49.3	42.0		57.4	54.9	56.2		222	220	(**)
High†	36.7	35.4	----		101.1	97.0	----		43.6	41.1	----		47.3	48.5	----		52.4	55.3	----		211	(**)	---
Type 430 SS																							
Control	----	----	----	71.6	62.5	62.5	64.4	53.5	33.8	34.0	35.6	30.3	35.3	34.0	34.0	67.7	72.0	73.3	78.1	107	110	113	129
Low*	20.2	21.1	38.7		64.0	65.1	63.9		35.4	36.3	36.4		33.0	37.0	32.0		68.3	73.5	83.6		124	124	130
High†	8.3	13.2	----		64.2	63.8	----		35.3	37.6	----		37.5	35.5	----		73.3	70.0	----		118	125	---
Inconel																							
Control	----	----	----	93.8	87.2	84.4	79.5	39.5	34.2	34.6	31.9	45.7	41.0	40.7	37.0	60.7	64.1	57.1	72.8	223	187	165	236
Low*	14.0	22.6	25.0		93.4	94.5	92.6		35.4	36.2	35.4		42.0	44.0	43.0		56.7	60.7	61.8		225	223	215
High†	36.6	55.5	----		93.9	93.0	----		36.1	34.5	----		40.5	42.0	----		50.3	54.9	----		214	221	---
Aluminized Inconel																							
Control	----	----	----	75.8	76.3	72.8	64.4	25.9	28.6	27.2	29.0	39.0	37.7	35.7	(**)	58.0	51.3	50.1	(**)	160	162	160	(**)
Low*	24.0	7.3	24.2		76.2	72.7	70.7		29.3	29.5	29.0		35.0	34.7	33.0		47.3	52.5	44.8		156	170	165
High†	18.2	32.4	----		75.0	68.7	----		28.0	26.3	----		34.0	37.5	----		54.7	55.7	----		164	167	---

* Material exposed to low-impurity-concentration helium (200 to 300 ppm CO and 200 to 300 ppm H₂).

† Material exposed to high-impurity-concentration helium (2000 to 3000 ppm CO and 2000 to 3000 ppm H₂).

** Not determined.

weight gains were noted because the weight gained by reaction was greater than the weight lost by vaporization.

All materials exposed at 1400°F to low-impurity helium, with the exception of 430 stainless steel (see Fig. 3), appeared to follow a rate law of the type

$$\Delta W = kt^n,$$

where ΔW is the weight gain, t is time, n is a constant whose value is less than one, and k is a proportionality constant. This implies that the reaction became less rapid the longer the exposure time; indeed, only slight gains in weight were noted between 1500 and 3000 hr of exposure. Type 430 stainless steel, however, exhibited an increasing rate of weight gain during this exposure interval.

All specimens exposed at 1200°F to high-impurity helium, with the exception of Type 304 stainless steel (see Fig. 4), showed a diminished rate of reaction at the longer exposure times. For exposures up to 1500 hr, the rate of weight gain for Type 304 stainless steel appeared to be linear.

For exposure times up to 1500 hr, the rate of weight gain appeared to diminish with increasing exposure times for all materials exposed at 1400°F to high-impurity helium (see Fig. 5). For Type 304 stainless steel, an additional measurement was obtained after 3000-hr exposure; the weight gain of 66.5 mg/dm² is only slightly above the value of 60.8 mg/dm² observed after 1500-hr exposure.

The influences of impurity concentration and temperature on weight gain are evident from the bar graphs in Figs. 6 and 7, which illustrate the weight gains after 1500 hr, the longest exposure time for which enough data are available for such a comparison. These data indicate that there is little variation in weight gain with impurity concentration for the austenitic stainless steels but a marked concentration-dependence for Inconel. The weight gains for Inconel and Type 430 stainless steel showed much less temperature-dependence than was observed for the other materials. Similar observations were made for the data obtained after 500-hr exposure.

Fig. 6--Weight gains due to exposure at 1200°F for 500 and 1500 hr

Fig. 7--Weight gains due to exposure at 1400°F for 1500 hr

Carbon Content

The carbon content of the exposed specimens is listed in Tables 4 and 5 and plotted in Figs. 8 and 9. A somewhat unexpected result is evident; many specimens which exhibited carburization during the first 500 hr of exposure exhibited decarburization after 1500-hr exposure. However, all of those specimens exposed at both temperatures to the lower impurity concentration exhibited an increase in their carbon content between 1500 and 3000 hr of exposure. Other investigators* have also observed alternating carburization and decarburization in stainless steels exposed to an environment of CO and H₂. Further evidence of this alternating carburization and decarburization was obtained by analyzing the carbon content of layers at different depths from the surface of specimens exposed for 1500 hr at 1400° F to the higher impurity concentration. The results for Type 347 stainless steel are illustrated in Fig. 10.

The highest carbon concentration observed for any of the specimens was 0.135 wt-% for Type 321H stainless steel, but since the carbon content was increasing at the conclusion of the 3000 hr of exposure, longer exposures would be required to determine if the carbon content continues to increase.

Oxidation Contribution to Weight Gain

Data representing total weight gains after 1500-hr exposure were utilized to determine the contribution to the weight change due to changes in carbon content and, by difference, the contribution due to oxidation. These data are presented in Figs. 11 through 14. It must be emphasized that these figures are plotted from data determined from individual specimens (those which were analyzed for carbon content), not average values, and these data were not normalized to a weight per unit area basis. Figures were not prepared for Type 430 stainless steel, since it exhibited no change in carbon content, nor for aluminized Inconel, since the previously discussed

* F. Eberle and R. D. Wylie, "Attack on Metals by Synthesis Gas from Methane-Oxygen Combustion," Corrosion, Vol. 15, 1959, pp. 622-626.

Table 4

CARBON CONTENT OF SPECIMENS EXPOSED TO HELIUM WITH LOW
IMPURITY CONCENTRATION (200-300 PPM CO
AND 200-300 PPM H₂)
(In wt-%)

Material	As Received	1200°F Exposure			1400°F Exposure		
		At 500 Hr	At 1500 Hr	At 3000 Hr	At 500 Hr	At 1500 Hr	At 3000 Hr
Type 321H SS	0.083	0.084	0.040	0.101	0.135	0.042	0.121
Type 347 SS	0.066	0.048	0.045	0.081	0.059	0.047	0.102
Type 304 SS	0.041	0.037	0.043	0.066	0.042	0.057	0.082
Type 430 SS	0.072	0.071	0.061	0.082	0.071	0.076	0.115
Inconel	0.038	0.048	0.016	0.044	0.044	0.025	0.076
Aluminized Inconel	0.038	0.042	0.017	0.035	0.048	0.032	0.046

Table 5

CARBON CONTENT OF SPECIMENS EXPOSED TO HELIUM WITH HIGH
IMPURITY CONCENTRATION (2000-3000 PPM CO
AND 2000-3000 PPM H₂)
(In wt-%)

Material	As Received	1200°F Exposure		1400°F Exposure	
		At 500 Hr	At 1500 Hr	At 500 Hr	At 1500 Hr
Type 321H SS	0.083	0.086	0.089	0.12	0.098
Type 347 SS	0.066	0.068	0.088	0.094	0.055
Type 304 SS	0.041	0.047	0.050	0.070	0.056
Type 430 SS	0.072	0.073	0.073	0.067	0.073
Inconel	0.038	0.037	0.045	0.050	0.040
Aluminized Inconel	0.038	0.035	0.039	0.026	0.014

Fig. 8--Carbon content of specimens exposed at 1200° and 1400°F to helium containing 200 to 300 ppm CO and 200 to 300 ppm H₂

Fig. 9--Carbon content of specimens exposed at 1200° and 1400°F to helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H₂

(a)

(b)

Fig. 10--Carbon content of Type 347 stainless steel exposed at 1400°F to helium containing 2000 to 3000 ppm CO and 2000 to 3000 ppm H₂ for 1500 hr (as-received carbon content of the stainless steel was 0.083%): (a) longitudinal distribution; (b) depth distribution

Fig. 11--Total weight gain of Type 304 stainless steel after 1500 hr exposure in controlled environments, showing oxygen and carbon contributions to weight gain

Fig. 12--Total weight gain of Type 321H stainless steel after 1500 hr exposure in controlled environments, showing oxygen and carbon contributions to weight gain

Fig. 13--Total weight gain of Type 347 stainless steel after 1500 hr exposure in controlled environments, showing oxygen and carbon contributions to weight gain

Fig. 14--Total weight gain of Inconel after 1500 hr exposure in controlled environments, showing oxygen and carbon contributions to weight gain

volatilization of the aluminum coating complicated any such analysis of the data. All of these figures indicate that changes in the carbon content contributed only a small amount to the total weight change and that the predominant corrosion mechanism appeared to be an oxidation process. Each of the materials exhibited some interesting characteristics:

Type 304 Stainless Steel. Slight carburization was exhibited after any of the above-mentioned exposures and did not appear to be dependent either on impurity concentration or on temperature. Oxidation was temperature- but not impurity-concentration-dependent and was responsible for the temperature-dependence of the total weight gain. Both carburization and oxidation appeared to have little time-dependence at 1500-hr exposure.

Type 321H Stainless Steel. Carburization was evidenced after 500-hr exposure, but the carbon content decreased after longer exposures. Carburization was dependent upon impurity concentration but not upon temperature. Oxidation was strongly temperature-dependent, but was only slightly impurity-concentration-dependent. At both temperatures, oxidation showed a linear dependence with time throughout the exposure period. Oxidation was responsible for the temperature-dependence exhibited by the total weight change.

Type 347 Stainless Steel. Changes in carbon content were more dependent upon impurity concentration than upon temperature. Oxidation was dependent upon both temperature and impurity concentration. After 1500-hr exposure, oxidation exhibited little time-dependence; however, the relationship between changes in carbon content and longer exposures was uncertain.

Inconel. Both oxidation and changes in carbon content appeared to be more closely related to changes in impurity concentration than in temperature. Further changes in both oxidation and carbon content could be expected with longer exposures.

X-ray Analyses of Reaction Products

A small number of samples exposed for 1500 hr to the higher impurity

concentration were subjected to X-ray diffraction analyses to identify the reaction products. These data, presented in Table 6, were not very extensive but serve to illustrate that oxidation appeared to be the primary corrosion mechanism. In no case was a carbide identified as a corrosion product.

Table 6

REACTION PRODUCTS IDENTIFIED BY X-RAY DIFFRACTION
ON SPECIMENS EXPOSED FOR 1500 HR TO HELIUM CONTAIN-
ING 2000-3000 PPM CO AND 2000-3000 PPM H₂

Material	Exposure Temperature (°F)	Corrosion Products Identified
Type 347 SS	1400	Spinel, Cr ₂ O ₃
Type 430 SS	1400	None
Inconel	1400	Cr ₂ O ₃
Type 304 SS	1400	Spinel, Cr ₂ O ₃ , α-Fe
Type 347 SS	1200	Spinel, α-Fe
Type 430 SS	1200	Cr ₂ O ₃
Inconel	1200	Cr ₂ O ₃
Type 321H SS	1200	None

Metallographic Examination

Specimens that had been subjected to each exposure condition were metallographically examined. Examinations of these specimens corroborated the decarburization, temperature-dependence, and concentration-dependence effects discussed above. That the primary nature of the corrosion mechanism was oxidation was also corroborated by observations of oxide layers on the surfaces of all the exposed specimens examined.

Two notable results of the examination were the following observations: (1) Copious quantities of precipitate formed at the grain boundaries

in the Type 321H stainless steel specimens exposed to the higher impurity concentration at 1400°F for 1500 hr (see Fig. 15) and in the specimens exposed for 3000 hr at either 1400° or 1200°F . (2) Cracks penetrated the aluminized coating after prolonged exposure of the Inconel at elevated temperatures (see Fig. 16). This cracking of the coating indicated that any protection the coating offered would be eliminated after long time exposures. The precipitate in the Type 321H stainless steel was related to an embrittling effect which was evident in analyses of the mechanical properties described in the next section.

Visual examination of the specimens after exposure for 1500 hr at 1400°F to the higher impurity concentration led to the observation that a number of the austenitic stainless steel specimens had a profusion of metallic-appearing nodules. These nodules appeared to be acting as nuclei for the growth of some phase, and in advanced stages large blisters were formed. These blisters did not appear to be adherent to the base metal. It was noted that those specimens exhibiting this phenomenon had much larger weight gains than those of similar specimens which did not show this reaction.

Metallographic examination showed that these blisters grew on an oxide substrate which formed on the specimen's surface; i. e., when a blister was stripped, the specimen surface appeared oxidized and was similar to the surface of specimens where the blisters did not appear. X-ray diffraction analyses identified the blisters as ferrite ($\alpha\text{-Fe}$), and this identification was verified by the magnetic nature of the blisters which were stripped from the specimens. No explanation for their formation is postulated.

Specimens of Type 304 stainless steel that were subjected to the same exposure conditions (1400°F , high impurity concentration) for 3000 hr did not have these nodules.

Mechanical Properties

The results of tensile and tensile-impact tests are shown in Figs. 17 through 28. Only one material, Type 321H stainless steel that was exposed

(500×)

Fig. 15--Type 321H stainless steel exposed for 1500 hr at 1400° F to helium containing 2000 to 3000 ppm H₂ and 2000 to 3000 ppm CO; note the precipitate formation at grain boundaries

(500×)

Fig. 16--Aluminized Inconel exposed for 3000 hr at 1200° F to helium containing 200 to 300 ppm H₂ and 200 to 300 ppm CO; note the cracks penetrating the coating

Fig. 17--Mechanical properties of Type 304 stainless steel exposed in controlled environments at 1200°F

Fig. 18--Mechanical properties of Type 304 stainless steel exposed in controlled environments at 1400°F

Fig. 19--Mechanical properties of Type 321H stainless steel exposed in controlled environments at 1200°F

Fig. 20--Mechanical properties of Type 321H stainless steel exposed in controlled environments at 1400°F

Fig. 21--Mechanical properties of Type 347 stainless steel exposed in controlled environments at 1200°F

Fig. 22--Mechanical properties of Type 347 stainless steel exposed in controlled environments at 1400°F

Fig. 23--Mechanical properties of Type 430 stainless steel exposed in controlled environments at 1200°F

Fig. 24--Mechanical properties of Type 430 stainless steel exposed in controlled environments at 1400°F

Fig. 25--Mechanical properties of aluminized Inconel exposed in controlled environments at 1200°F

Fig. 26--Mechanical properties of aluminized Inconel exposed in controlled environments at 1400°F

Fig. 27--Mechanical properties of Inconel exposed in controlled environments at 1200°F

Fig. 28--Mechanical properties of Inconel exposed in controlled environments at 1400°F

to the higher impurity concentration for 1500 hr at 1400°F, showed a drastic decrease in elongation and in reduction of area (see Table 3). The mode of fracture also changed from 100% shear to primarily intercrystalline failure. This material, therefore, could not be considered for structural applications under these exposure conditions.

No other material tested exhibited a severe reduction in ductility or toughness, even after 3000-hr exposure in the lower impurity concentration (see Tables 2 and 3). In fact, in some cases the ductility after 3000-hr exposure to the low-impurity-concentration helium was greater than the initial ductility.

SUMMARY AND CONCLUSIONS

Specimens of six structural materials were exposed for times up to 3000 hr to the following environmental conditions: temperatures of 1200°F or 1400°F and atmospheres of helium containing either 200 to 300 ppm H₂ and 200 to 300 ppm CO or 2000 to 3000 ppm H₂ and 2000 to 3000 ppm CO. Under these experimental exposure conditions, oxidation rather than carburization appeared to be the major corrosion process influencing the materials studied. However, in some cases alternating carburization and decarburization were observed. In no case did the carbon content of any material studied exceed 0.135 wt-%. Coating Inconel with aluminum was of little protective value, as the coating offered no protection from either carburization or decarburization and exhibited cracking after long time exposures.

Measurements of the weight gain of specimens subjected to both the low and the high impurity concentrations at 1200°F for times up to 1500 hr showed that a parabolic rate law was followed for all six materials. However, extending the exposure times to 3000 hr for specimens exposed to the lower impurity concentration showed an increasing rate of weight gain for all stainless steels with increasing exposure times between 1500 and 3000 hr.

Materials exposed at 1400°F to both impurity concentrations followed a parabolic rate law, with the exception of Type 430 stainless steel. The

latter material showed an increase in the rate of weight gain between 1500 and 3000 hr.

Measurements of tensile and tensile-impact properties of the exposed and the control specimens illustrated that only one material, Type 321H stainless steel, suffered a severe loss of ductility as a result of these treatments.

With the exception of Type 321H stainless steel, none of the materials studied were observed to suffer serious changes in their mechanical properties after exposures to the simulated reactor environments investigated. Results for the various materials studied can be summarized as follows:

Ferritic Stainless Steel

Type 430 stainless steel exhibited no deleterious change in mechanical properties under the exposure conditions; however, the rate of weight loss began to increase at exposure times greater than 1500 hr. It is well known that this steel exhibits susceptibility to sigma-phase embrittlement and 885°F embrittlement under longer times of exposure.

Austenitic Stainless Steel

With the exception of Type 321H stainless steel, the types of this class of steel that were studied (Types 304 and 347) look quite promising for these applications. The following observations should be considered, however:

1. The increasing rate of weight gain for long time exposures at 1200°F.
2. The still-changing mechanical properties of Type 304 stainless steel even after 3000-hr exposure at 1400°F (although this material exhibited adequate ductility after 3000-hr exposure).
3. The appearance of ferrite nodules on these steels after 1500-hr exposure to the higher impurity concentration.

Nickel Base Alloy

The results of tests with Inconel were as follows:

1. Weight gains appeared to be saturating at the longer exposure times studied.

2. Weight gains of Inconel were the least temperature-dependent of the materials tested.
3. The carbon content after 3000-hr exposure was lower than the carbon content in the stainless steels exposed under similar conditions.
4. Mechanical properties were only slightly changed after 3000-hr exposure.

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