Effects of Oxidation on the Impact Energy of Hastelloy S and Hastelloy C-4 Charpy V-Notch Specimens Heated in Air at 600° to 800°C

H. T. Fullam

January 1981

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$ _____ *: Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00056 1581

EFFECTS OF OXIDATION ON THE IMPACT ENERGY OF
HASTELLOY S AND HASTELLOY C-4 CHARPY V-NOTCH
SPECIMENS HEATED IN AIR AT 600° to 800°C

H. T. Fullam

January 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

A program is under way at the Pacific Northwest Laboratory to develop a general-purpose radioisotope heat source fueled with $^{90}\text{SrF}_2$ for terrestrial applications. The work is funded by the Advanced Nuclear Systems and Projects Division of the Department of Energy.

The heat source design utilizes a Hastelloy C-276 inner capsule to contain the $^{90}\text{SrF}_2$ and a Hastelloy S (or Hastelloy C-4) outer capsule to provide the structural strength needed to meet licensing requirements. One of the design requirements for the heat source is that the outer capsule must be resistant enough to oxidation that 10 years of service in air at temperatures up to 800°C would not degrade the structural strength of the capsule below licensing requirements. The design calls for the outer capsule to have an outer diameter of 3.375 in. and a wall thickness of 0.500 in.

Studies were carried out to measure the oxidation of Hastelloy S and Hastelloy C-4 in air at 600° to 800°C for times up to 10,000 h and to determine what effects the oxidation had on the tensile strength and Charpy impact energy of test specimens fabricated from the two alloys. Detailed information on oxidation rates, oxide compositions, and the effects of oxidation on tensile properties was provided in PNL-3344 (Fullam 1980). This report discusses the effects of oxidation on the Charpy impact energy of Hastelloy S and Hastelloy C-4 specimens.

Hastelloy S and Hastelloy C-4 Charpy V-notch (CVN) specimens were heated in air or vacuum at 600° , 700° and 800°C for up to 10,000 h. The specimens were then impact-tested at room temperature. The CVN specimens were subsize specimens prepared in accordance with ASTM specification E23-72 (Anon. 1978). The specimens were fabricated from 0.125-in. alloy sheets, and were oriented with the notch parallel to the rolling direction and perpendicular to the surface of the sheet.

Oxidation of Hastelloy S and Hastelloy C-4 in air is very slow at 600° to 800°C and both alloys form adherent oxide layers that serve to protect the underlying metal. There was no evidence of breakaway spalling during oxidation, but spalling did occur with some specimens after they were removed from the hot furnaces and cooled to room temperature. Oxidation of the two alloys adhered to parabolic rate relationships for exposures of up to 5000 h. Longer exposures led to negative deviations from the parabolic rates. Conservative estimates of long-term oxidation can be made using the parabolic rate equations developed from the short-term (up to 10,000 h) data.

Subsurface attack of the Hastelloy S and Hastelloy C-4 due to oxidation was estimated from photomicrographs of the oxidized test specimens. Specimens oxidized at 600° to 800°C for up to 10,000 h suffered subsurface attack to depths up to $55\text{ }\mu\text{m}$ ($\sim 0.002\text{ in.}$), which corresponded to about 5.7% of the cross-sectional area below the notch of the CVN specimens. The data were erratic, however, making it difficult to determine the rate equations for subsurface attack. A very conservative estimate of long-term subsurface attack can be made using a linear extrapolation of the short-term test results.

The Hastelloy S and Hastelloy C-4 CVN specimens that had been aged in air or vacuum at 600^o to 800^oC were impact-tested at room temperature. A statistical analysis of the test results showed there was no significant difference between the Charpy impact energy of the specimens aged in air and the control specimens aged in a vacuum. This was true even though the subsurface attack due to oxidation affected up to 5.7% of the cross-sectional area of the CVN specimens. The CVN specimens aged at 600^oC showed the greatest reduction in room-temperature Charpy impact energy. Higher aging temperatures had less effect on the Charpy impact energy of the two alloys, and the Hastelloy S specimens aged at 800^oC actually exhibited a higher Charpy impact energy than the solution heat-treated alloy.

Extrapolation of the test results shows that oxidation of a Hastelloy S or Hastelloy C-4 outer capsule in air at temperatures up to 800^oC for up to 10 years would result in subsurface attack to a depth of about 0.013 in. This means that approximately 3% of the cross-sectional area of the capsule would be affected by subsurface attack. Based on the short-term test results, this degree of attack should not have a significant effect on the impact strength of the capsule.

CONTENTS

SUMMARY	iii
1.0 INTRODUCTION	1
1.1 LICENSING REQUIREMENTS FOR A $^{90}\text{SrF}_2$ HEAT SOURCE TO BE USED IN TERRESTRIAL APPLICATIONS	1
1.2 ADDITIONAL PNL AND DOE HEAT-SOURCE REQUIREMENTS	2
2.0 OBJECTIVES	5
3.0 PREVIOUS WORK	7
4.0 EXPERIMENTAL	11
5.0 RESULTS AND DISCUSSION	13
5.1 OXIDATION	13
5.2 CHARPY IMPACT ENERGY	17
5.3 EFFECTS OF LONG-TERM OXIDATION	20
6.0 CONCLUSIONS	25
REFERENCES	27
ACKNOWLEDGMENTS	29

FIGURES

1	The Oxidation of Hastelloy S in Air	14
2	The Oxidation of Hastelloy C-4 in Air	14
3	Hastelloy S and Hastelloy C-4 Specimens Oxidized in Air for 10,000 h	15
4	The Microstructure of Solution Heat-Treated Hastelloy S and Hastelloy C-4	16
5	The Room-Temperature Charpy Impact Energy of Hastelloy S Specimens Heated in Air or Vacuum	20
6	The Room-Temperature Charpy Impact Energy of Hastelloy C-4 Specimens Heated in Air or Vacuum	21
7	Effect of Thermal Aging on the Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4--Full-Size Specimens	22
8	Effect of Aging Temperature on the Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4	23
9	Estimates of the Depth of Metal Affected When Hastelloy C-4 is Oxidized in Air at 600° to 800°C	24
10	Estimates of the Depth of Metal Affected When Hastelloy S is Oxidized in Air at 600° to 800°C	24

TABLES

1	Depth of Metal Affected When Hastelloy S and Hastelloy C-4 Specimens Were Oxidized in Air at 600° to 800°C	8
2	The Composition and Mechanical Properties of the Hastelloy S and Hastelloy C-4 Used in Fabricating the Charpy V-Notch Specimens	12
3	Oxidation of Hastelloy S and Hastelloy C-4 in Air	13
4	Subsurface Attack of Hastelloy S and Hastelloy C-4 Specimens Oxidized in Air	18
5	The Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4 CVN Specimens Heated in Air or Vacuum	19

1.0 INTRODUCTION

A program is under way at the Pacific Northwest Laboratory (PNL)^(a) to develop the technology needed to permit the use of $^{90}\text{SrF}_2$ as a radioisotope heat-source fuel for terrestrial applications. The work is funded by the Advanced Nuclear Systems and Projects Division of the Department of Energy (DOE).

As part of the DOE waste management program at Hanford, ^{90}Sr is recovered from the stored high-level fuel-reprocessing wastes, purified, converted to $^{90}\text{SrF}_2$, and doubly encapsulated in metal canisters for subsequent storage in a water basin on the Hanford Reservation. The $^{90}\text{SrF}_2$ storage capsule consists of a Hastelloy Alloy C-276[®] inner canister and a 316L stainless steel outer canister. Preparation, encapsulation and storage of the $^{90}\text{SrF}_2$ takes place in the Waste Encapsulation and Storage Facility (WESF), which is operated for DOE by Rockwell International (RHO).

The stored $^{90}\text{SrF}_2$ represents a readily available source of radioisotope heat if the fluoride fuel form is approved for terrestrial use by the cognizant regulatory agencies. Unfortunately, the WESF $^{90}\text{SrF}_2$ storage capsule, which is completely adequate for its intended purpose, is not able to meet the licensing requirements for radioisotope heat sources to be used in terrestrial applications. Consequently, one objective of the current PNL program is to design and qualification-test a $^{90}\text{SrF}_2$ heat source that is capable of meeting current licensing requirements. By DOE directive the new heat source design is to utilize the existing Hastelloy C-276 inner capsule from the WESF $^{90}\text{SrF}_2$ storage capsule in combination with a new outer capsule. The design philosophy is that the Hastelloy C-276 inner capsule would serve as the primary containment barrier for the $^{90}\text{SrF}_2$, while the new outer capsule would provide the structural strength needed to meet the licensing requirements.

1.1 LICENSING REQUIREMENTS FOR A $^{90}\text{SrF}_2$ HEAT SOURCE TO BE USED IN TERRESTRIAL APPLICATIONS

The current requirements that the heat source must meet to be licensable for terrestrial use are spelled out in various regulations set forth by the Nuclear Regulatory Commission (NRC) and the International Atomic Energy Agency (IAEA) and are summarized below.^(b)

- The heat source capsule shall not leak at a rate greater than 10^{-8} std cm³/s after being subjected to an external pressure of 14,500 psi (1000 bar).
- The capsule shall not leak at a rate greater than 10^{-8} std cm³/s when dropped from a height of 9 m (approximately 30 ft) onto a steel plate at least 1.25 cm (approximately 1/2 in.) thick that has been wet-floated onto a concrete block with a mass of at least 10 times that of the capsule and set on firm soil. The steel plate shall be flat and

(a) Operated by Battelle Memorial Institute for the Department of Energy.

(b) Based on current NRC and IAEA regulations as defined in USAEC Regulatory Guide 6.3 (United States 1974) IAEA Safety Series 33 (IAEA 1970) and 10 CFR Parts 20 and 71 (Anon. 1979).

[®] Cabot Corp., Kokomo, Indiana.

horizontal and the capsule shall be dropped in such a manner that the maximum possible damage will result.

- The capsule shall not leak at a rate greater than 10^{-8} std cm³/s after being struck by the flat face of a 2.5-cm-dia (approximately 1-in.) steel billet with an impact energy equivalent to 7 kg-m (approximately 50 ft-lb). The billet edges shall be rounded off to a radius of not less than 3 mm, and the capsule shall rest on a lead sheet equal to or less than 25 mm thick with a Brinell hardness of 3.5 to 4.5. The lead sheet shall cover a greater area than the capsule and shall rest on a smooth, solid surface. A fresh lead sheet shall be used for each test, and the capsule shall be struck in such a manner that the maximum possible damage will result.
- The capsule shall not leak at a rate greater than 10^{-8} std cm³/s after being heated to its maximum operating temperature of 800°C and held at 800°C for 30 min.
- The capsule shall not leak at a rate greater than 10^{-8} std cm³/s after being heated to its maximum operating temperature of 800°C and then plunged into a water-ethylene glycol solution at 32°F (0°C). The capsule shall remain for 1 hour in the circulating solution, which shall at no time exceed 41°F (5°C).
- The capsule shall pass a test (experimental and/or thermal analysis) such that the capsule remains capable of fuel containment during and after a 30-min fire at 1475°F (802°C). The outer capsule shall contain either a standard WESF ⁹⁰SrF₂ inner capsule or the equivalent fuel (as SrF₂) contained in the WESF inner capsule, whichever condition is worse, and shall receive no supplemental cooling after the fire. The test (or calculation) shall be continued until no further material damage due to increasing temperature and/or accelerated fuel/encapsulation material reactions at elevated temperature is possible.

1.2 ADDITIONAL PNL AND DOE HEAT-SOURCE REQUIREMENTS

In addition to the NRC/IAEA standards, DOE and PNL have defined additional requirements for the heat source to improve its usefulness and enhance its safe utilization. The additional requirements include the following:

- The outer capsule of the ⁹⁰SrF₂ heat source must meet the licensing requirements given in Section 1.1 in both the as-fabricated and post-serve conditions without support from the inner capsule.
- The outer capsule of the ⁹⁰SrF₂ heat source must be sufficiently resistant to corrosion that air oxidation occurring during the normal service life of the heat source will not degrade the properties of the capsule below the NRC/IAEA licensing requirements. The oxidation requirement for the capsule is based on the conditions that:
 - a. The outer capsule surface temperature will not exceed 800°C
 - b. The service life of the heat source will not exceed 10 years.

The ability of the capsule to meet the oxidation requirement may be demonstrated by the extrapolation of reliable short-term oxidation data using established procedures.

These requirements mean that the outer capsule must be capable of meeting the licensing criteria despite the degradation in mechanical properties the capsule material would suffer due to long-term thermal-aging reactions and air oxidation.

Hastelloy Alloy S® has been selected as the outer capsule material, with Hastelloy Alloy C-4® as the secondary choice in case the Hastelloy Alloy S has to be rejected for any reason. Cabot Corp. has reported that both alloys suffer a loss of ductility and Charpy impact strength due to microstructural changes when they are heated at 400 to 900°C for extended periods of time (Matthews 1976). However, the degradation in ductility and Charpy impact strength of Hastelloy S and Hastelloy C-4 due to the thermal-aging reactions is less than occurs with most oxidation-resistant superalloys; this was the primary reason for selecting Hastelloy S for the outer capsule material and Hastelloy C-4 as the backup material. The design of the outer capsule (Simonen, Shippel, Jr. and Atteridge 1980; Simonen and Shippel, Jr. 1980), which calls for a 0.5-in. capsule wall thickness, was based on the data reported by Cabot Corp. for the thermally aged Hastelloy S (Matthews 1976). Studies were carried out at PNL to obtain additional data on the effects of thermal aging reactions on the mechanical properties of the two alloys, and on the potential effects of air oxidation at heat-source operating temperatures (600° to 800°C) on the structural properties of the heat-source outer capsule. The data obtained on the effects of oxidation and thermal-aging reactions on the tensile properties of Hastelloy S and Hastelloy C-4 was reported in PNL-3344 (Fullam 1980), while this report discusses their effects on the Charpy impact strengths of the two alloys.

® Cabot Corp., Kokomo, Indiana

2.0 OBJECTIVES

The $^{90}\text{SrF}_2$ heat source being developed at PNL utilizes a Hastelloy S or Hastelloy C-4 outer capsule having a 0.5-in.-thick wall to contain the Hastelloy C-276 inner capsule. The primary objective of the study was to demonstrate that the air oxidation of the outer capsule that could occur during heat-source service would not degrade the ductility and Charpy impact strength of the capsule below the licensing requirements given in Section 1.1.

The $^{90}\text{SrF}_2$ heat source under development is intended for general-purpose use. Compatibility considerations limit the interface temperature between the $^{90}\text{SrF}_2$ and Hastelloy C-276 inner capsule to a maximum of 800°C . The outer capsule surface temperature will be somewhat less than 800°C , and depending on the service, may be substantially lower. The oxidation tests were therefore carried out at 600° to 800°C to cover the range of temperature the outer capsule might expect to encounter in service.

3.0 PREVIOUS WORK

The oxidation of Hastelloy S and Hastelloy C-4 in air was measured at 600° to 800°C for exposures up to 10,000 h and the effect of the oxidation on the tensile properties of the two alloys determined (Fullam 1980). The results obtained show that the rate of oxidation of both alloys in air is very slow at 600° to 800°C, and they form adherent oxide layers that serve to protect the underlying metal. Over the temperature range studied, the oxidation of Hastelloy S and Hastelloy C-4 in air adhered to parabolic rate relationships, except for initial deviations, for exposures up to 5000 h. Longer exposures resulted in negative deviations, from the parabolic rate relationships. There was no evidence of breakaway spalling of the oxide layers during heating, but some spalling did occur with some test specimens during cooling after the specimens were removed from the hot furnaces.

The parabolic rate relationships for the oxidation of the two alloys in air are given by the following equations:

Hastelloy S

$$\begin{array}{ll} 600^{\circ}\text{C}, & \Delta w^2 = 1.64 \times 10^{-6} T + 0.00498 \\ 700^{\circ}\text{C}, & \Delta w^2 = 2.26 \times 10^{-5} T + 0.00767 \\ 800^{\circ}\text{C}, & \Delta w^2 = 5.73 \times 10^{-5} T + 0.0277 \end{array}$$

Hastelloy C-4

$$\begin{array}{ll} 600^{\circ}\text{C}, & \Delta w^2 = 1.92 \times 10^{-5} T + 0.154 \\ 700^{\circ}\text{C}, & \Delta w^2 = 3.34 \times 10^{-5} T + 0.221 \\ 800^{\circ}\text{C}, & \Delta w^2 = 8.19 \times 10^{-5} T + 0.271 \end{array}$$

where

Δw = weight gain per unit area, mg/cm²

T = time, h.

Because exposures longer than 2500 to 5000 h lead to negative deviations from the parabolic rate relationships, the equations given above can be used to make conservative estimates of the long-term oxidation of Hastelloy S and Hastelloy C-4.

It was found that subsurface attack of the Hastelloy S and Hastelloy C-4 due to oxidation was greater than one would predict from the weight-gain data. Microstructural changes, depletion of alloy constituents, grain-boundary attack, pitting, etc., occurred to considerable depths with both alloys when they were heated in air at 600° to 800°C. It is the subsurface attack that could affect the mechanical properties of the heat source outer capsule. Table 1 shows the depth of metal affected by the oxidation reactions when Hastelloy S and Hastelloy C-4 were heated in air. The data are so erratic it is impossible to determine what type of rate equation applies to each alloy at the different temperatures. The best estimate that can be made is that the rate in each case is less than linear and probably closer to parabolic or exponential.

TABLE 1. Depth of Metal Affected When Hastelloy S and Hastelloy C-4 Specimens Were Oxidized in Air at 600° to 800°C

Temperature, °C	Time, h	Depth of Metal Affected, μm	
		Hastelloy S	Hastelloy C-4
600	140	13	8
	300	15	12
	528	17	15
	994	14	10
	2,500	18	16
	5,000	20	18
	7,500	26	23
	10,000	30	30
700	140	7	6
	300	8	8
	528	10	13
	994	10	8
	2,500	18	18
	5,000	15	20
	7,500	20	20
	10,000	18	25
800	140	14	10
	300	16	12
	528	20	13
	994	16	16
	2,500	23	23
	5,000	30	15
	7,500	42	36
	10,000	50	40

Subsize tensile specimens (0.113 in. in dia) of Hastelloy S and Hastelloy C-4 were heated in air and vacuum at 600°, 700° and 800°C for up to 10,000 h. When the tensile specimens were tension-tested at room temperature, no significant differences were observed between the specimens heated in air and the control specimens heated in vacuum. The Hastelloy S tensile specimens heated in air at 800°C for 10,000 h suffered subsurface attack to a depth of 50 μm (~ 0.002 in.), which represented approximately 7% of the cross-sectional area of the specimens. Even this degree of subsurface attack did not affect the tensile strength of the oxidized specimens. The heat-source outer capsule must be able to withstand 10 years' oxidation at 800°C without a significant degradation in tensile strength. A very conservative estimate of long-term subsurface attack can be made using a linear extrapolation of data given in Table 1. Such an extrapolation shows that Hastelloy S oxidized in air at 800°C for 10 years would suffer subsurface attack to a depth of about 335 μm (~ 0.013 in.). For the heat-source outer capsule, which has an ID of 2.375 in. and an OD of 3.375 in., this degree of attack

would amount to only about 3% of the cross-sectional area of the capsule. Since the tensile specimens that suffered subsurface attack over 7% of their cross-sectional area exhibited no loss of tensile strength, the Hastelloy S heat-source outer capsule should suffer no significant loss of tensile strength when oxidized in air at 800°C for 10 years. Similar calculations show that a Hastelloy C-4 outer capsule should not suffer a significant loss of tensile strength when heated in air at 800°C for 10 years.

4.0 EXPERIMENTAL

Hastelloy S and Hastelloy C-4 Charpy V-notch (CVN) impact specimens were heated in air or vacuum at 600⁰, 700⁰ and 800⁰C for various times up to 10,000 h. After the heating cycle, the specimen were impact-tested at room temperature. Duplicate specimens were tested for each set of conditions.

The CVN specimens were subsize specimens 0.098 in. thick by 0.394 in. wide and were fabricated in accordance with ASTM Specification E23-72 (Anon. 1978). All specimens were cut from alloy sheet with the specimen notch oriented parallel to the rolling direction and perpendicular to the surface of the sheet. Subsize specimens were used to emphasize the possible effects of air oxidation on Charpy impact energy of the two alloys; since the fraction of the cross-sectional area affected by subsurface oxidation reactions are greater for subsize specimens than for full-size specimens.

The Hastelloy S specimens were fabricated from 0.125-in. sheet that had been solution heat-treated at 1950⁰F and air-cooled. The Hastelloy C-4 specimens were cut from 0.125-in. sheet that had been solution heat-treated at 1950⁰F and rapid-quenched. The compositions and mechanical properties of the two alloys are given in Table 2.

After fabrication, the specimens were thoroughly cleaned, their dimensions determined to 0.001 in., and they were weighed on a semimicrobalance (± 0.01 -mg sensitivity). The specimens that were to serve as controls were doubly encapsulated in evacuated quartz envelopes to prevent oxidation during the heating cycle.

The specimens were heated in air-atmosphere muffle furnaces equipped with solid-state proportioning controllers capable of maintaining the temperature within $\pm 2^{\circ}\text{C}$ of the set point. Each furnace was equipped with thermocouple break protection and two separate and independent overtemperature-protection (OTP) circuits to prevent overheating in case of controller failure. The OTP circuits were set to shut off power to the furnace if the temperature exceeded the control temperature by more than 10⁰C.

The oxidation tests lasted 1,000, 2,500, 5,000, 7,500 and 10,000 h. All of the specimens were placed in a furnace at one time and heated to the desired temperature. At the prescribed intervals the specimens were removed from the hot furnace and allowed to cool to room temperature. As the specimens were removed from the furnaces they were examined visually for any evidence of spalling of the oxide layer. After the specimens had cooled they were reweighed and their dimensions determined. The control specimens were removed from quartz envelopes and treated in a similar manner. All of the specimens were then impact-tested at room temperature and a number of the failed specimens were subjected to metallographic examination. Oxidation rates were determined from the weight-change data, and subsurface attack of the specimens due to oxidation was estimated from the photomicrographs of the failed specimens.

TABLE 2. The Composition and Mechanical Properties of the Hastelloy S and Hastelloy C-4 Used in Fabricating the Charpy V-Notch Specimens(a)

<u>Alloy Characteristics</u>	<u>Hastelloy S--0.125 in. Sheet, Solution Heat- Treated @ 1950 F</u>	<u>Hastelloy C-4--0.125-in. Sheet, Solution Heat, Treated @ 1950 F</u>
<u>Element</u>	<u>Comp., wt%</u>	<u>Comp., wt%</u>
Al	0.16	
B	0.004	
C	0.006	0.003
Co	0.59	0.44
Cr	16.12	15.75
Cu	0.08	
Fe	1.88	1.10
La	0.013	
Mn	0.71	0.08
Mo	14.59	15.25
Ni	Bal	Bal
P	0.005	0.008
S	0.005	0.007
Si	0.33	0.02
Ti		0.23
W	0.27	
<u>Tensile Properties and Units</u>	<u>Values</u>	<u>Values</u>
Ultimate Tensile Strength, MPa	889	769
Yield Strength, MPa	476	358
% Elong., in 2 in.	48.6	58.0

(a) Based on the certified reports of chemical analysis and mechanical tests supplied by the manufacturer.

5.0 RESULTS AND DISCUSSION

5.1 OXIDATION

The oxidation of Hastelloy S and Hastelloy C-4 Charpy impact specimens in air was measured at 600^o, 700^o and 800^oC for exposures up to 10,000 h. Both alloys formed adherent oxide layers and there was no evidence of breakaway spalling of the oxide layers during heating. Spalling did occur with some specimens when they were removed from the hot furnaces and cooled to room temperature. There were no discernible changes in the dimensions of the specimens due to formation of the oxide layers.

The rate of oxidation of the Hastelloy S and Hastelloy C-4 impact specimens in air was determined using the discontinuous gravimetric procedure described in Section 4.0. The results obtained are summarized in Table 3. If the weight-gain data presented in Table 3 are plotted as Δw^2 against time, the results shown in Figures 1 and 2 are obtained. The straight lines shown in the figures are the parabolic oxidation rates given by the equations presented in Section 3.0. The data show that oxidation of the impact specimens agreed with the parabolic rate equations for exposures of up to 5000 h. Longer exposures led to negative deviations from the parabolic rate relationships. Similar results were obtained in the earlier oxidation studies.

All of the data show that oxidation of Hastelloy S and Hastelloy C-4 in air is very slow at 600^o to 800^oC, and the two alloys are among the most oxidation-resistant of the nickel-base alloys. A detailed discussion of Hastelloy S and Hastelloy C-4 oxidation, including compositions of the oxide layers and the probable reactions involved, are given in PNL-3344 (Fullam 1980).

After the oxidized CVN specimens were impact-tested at room temperature, a number of the failed specimens were subjected to metallographic examination. Figure 3 shows micrographs of the specimens that had been heated in air for 10,000 h. Figure 4 shows the microstructure of the solution heat-treated alloys as received from the vendor.

TABLE 3. Oxidation of Hastelloy S and Hastelloy C-4 in Air

Time, h	Average Specimen Weight Gain ^(a) ΔW , mg/cm ²					
	Hastelloy S			Hastelloy C-4		
	600 ^o C	700 ^o C	800 ^o C	600 ^o C	700 ^o C	800 ^o C
1,000	0.074	0.182	0.281			
2,500	0.099	0.245	0.406	0.449	0.552	0.694
5,000	0.109	0.342	0.550	0.505	0.617	0.758
7,500	0.111	0.363	0.598	0.520	0.620	0.869
10,000	0.105	0.362	0.658	0.501	0.679	0.887

(a) Average for duplicate specimens.

FIGURE 1. The Oxidation of Hastelloy S in Air

FIGURE 2. The Oxidation of Hastelloy C-4 in Air

FIGURE 3. Hastelloy S and Hastelloy C-4 Specimens Oxidized in Air for 10,000 h

HASTELLOY S

**SOLUTION HEAT-TREATED
AT 1950°F AND AIR-COOLED**

50 μm

HASTELLOY C-4

**SOLUTION HEAT-TREATED AT
1950°F AND RAPID-QUENCHED**

FIGURE 4. The Microstructure of Solution Heat-Treated Hastelloy S and Hastelloy C-4

Aging of Hastelloy S at 600°C results in an A_2B (Ni_2CrMo) long-range ordering reaction and precipitation of boride (M_3B_2) and carbide (M_6C) phases (Matthews 1976). A semicontinuous network of grain-boundary precipitates is formed and intragranular precipitation occurs. Aging of the Hastelloy S at 700°C and 800°C produces boride and carbide precipitates, but the A_2B ordering reactions does not occur. At 700°C a semicontinuous network of grain-boundary precipitates is formed, but at 800°C the precipitates form as discrete globules. When the Has-

Hastelloy S was heated in air at 600°C, subsurface attack produced a reaction zone in which the precipitates were largely depleted and the morphology appeared to have been altered. Oxidation at 700°C produced some pitting and grain-boundary attack and a narrow zone in which the normal precipitates were largely absent. Oxidation at 800°C resulted in more extensive pitting and grain-boundary attack and a much broader zone that was free of precipitates.

When Hastelloy C-4 is aged at 600°C it also undergoes a long-range ordering reaction and titanium nitride precipitates are formed, but no carbides or borides precipitate (Matthews 1976). The long-range ordering reaction is also reported to occur at 700°C but not at 800°C. The long-range ordering at 700°C was observed in the earlier PNL work (Fullam 1980), but in the current work the micrographs of the specimens aged at 700°C and 800°C show no evidence of the long-range ordering. No reasons have been identified for the differences in the 700°C results. Precipitation of Mu phase was observed at 700°C and 800°C, as was reported by Matthews. At 700°C the precipitates formed a semicontinuous grain-boundary network, while the precipitates were more agglomerated at 800°C.

When Hastelloy C-4 was heated in air at 600°C, a very narrow zone that was free of precipitates and whose morphology appeared to have been altered formed immediately beneath the oxide layer. Beneath this was a much wider zone, which appeared to be very heavily aged. Oxidation in air at 700°C produced some pitting and grain-boundary attack. In addition, there was a broad zone in which the grain size was much smaller than normal, and the grain-boundary precipitates were less evident. Oxidation of Hastelloy C-4 at 800°C resulted in more extensive pitting and grain-boundary attack and a broad zone in which the normal precipitates were partially depleted.

The depth of metal affected by the oxidation reactions is greater than one would predict from the weight-gain measurements. With some specimens it was difficult to determine from the photomicrographs the depth to which the metal was affected by oxidation. Estimates of the attack are given in Table 4. The data are very erratic and it is difficult to determine what type of rate equation applies. The most conservative approach is to assume that subsurface attack proceeds at a linear rate. At 800°C the subsurface attack affected the two alloys to depths up to 55 μm (about 0.002 in.). This means that up to 5.7% of the subsize CVN specimens' cross-sectional area below the notch was affected by this subsurface attack.

5.2 CHARPY IMPACT ENERGY

The Hastelloy S and Hastelloy C-4 CVN specimens that had been heated in air or vacuum were impact-tested at room temperature. The results obtained are presented in Table 5 and Figures 5 and 6. A cursory examination of the data indicates that the specimens heated in air at 700°C and 800°C exhibit a slightly higher room-temperature Charpy impact energy than do the control specimens heated in vacuum. A statistical analyses of the data shows, however, that there are no significant differences between the results obtained with the oxidized specimens and the control specimens heated in vacuum. This means that subsurface attack of the two

TABLE 4. Subsurface Attack of Hastelloy S and Hastelloy C-4 Specimens Oxidized in Air

Temp., °C	Time, h	Depth of Metal Affected, (a) μm	
		Hastelloy S	Hastelloy C-4
600	1,000	18	
	2,500		15
	5,000	20	25
	10,000	25	20
700	1,000	20	
	2,500		22
	5,000	25	32
	10,000	20	50
800	1,000	18	
	2,500		25
	5,000	38	45
	10,000	50	55

(a) Estimated from photomicrographs of oxidized specimens.

alloys due to oxidation (which affected up to 5.7% of the cross-sectional area of the CVN specimens) had no significant effect on their impact energy.

Both Hastelloy S and Hastelloy C-4 showed the greatest reduction in impact energy when aged at 600°C. Hastelloy S continued to show a gradual decrease in impact energy after 10,000-h exposure, whereas the impact energy of Hastelloy C-4 appeared to have reached a minimum after about 2500-h exposure.

Both alloys showed a decrease in impact energy when aged at 700°C. The data are quite erratic at 700°C, but it appears that the impact energy of Hastelloy S is continuing to decrease gradually after 10,000 h of exposure, while that of Hastelloy C-4 has stabilized.

When Hastelloy C-4 was aged at 800°C it showed a slight reduction in impact energy, except for the specimens that had been aged in air for 2500 h. These specimens exhibited an increase in impact energy. Metallographic examination of the oxidized specimens provided no indication of why their impact energy was markedly higher than that of the other specimens aged at 800°C. The Hastelloy S specimens aged at 800°C showed an increase in impact energy compared to the solution heat-treated alloy. The aged specimens exhibited a somewhat larger grain size than the solution heat-treated material, which could account for the increase in impact energy.

The temperature effects observed in this study are significantly different from the results reported by Cabot Corp. (Matthews 1976), although comparisons are difficult because the Cabot study used full-size Charpy specimens. Figure 7 shows the results obtained by

TABLE 5. The Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4 CVN Specimens Heated in Air or Vacuum

Temp., °C	Time, h	Charpy Impact Energy, ^(a) ft-lb			
		Hastelloy S		Hastelloy C-4	
		Vacuum	Air	Vacuum	Air
As-Received ^(b)		(14.0)		(29.5)	
600	1,000	10.1	9.8		
	2,500	8.7	8.7	8.7	8.0
	5,000	7.6	7.2	8.4	8.0
	7,500	6.5	7.2	7.6	7.2
	10,000	5.8	6.2	8.0	7.2
700	1,000	9.4	10.9		
	2,500	10.5	11.6	23.9	23.9
	5,000	11.6	10.9	19.5	22.5
	7,500	8.7	10.5	23.3	24.0
	10,000	10.1	10.1	23.8	25.0
800	1,000	15.5	16.3		
	2,500	15.5	16.5	25.8	32.8
	5,000	16.3	16.5	29.0	28.5
	7,500	15.5	16.3	27.5	28.3
	10,000	16.5	17.0	26.8	29.0

(a) Average value for duplicate specimens, except for as-received values where six Hastelloy S and five Hastelloy C-4 specimens were tested.

(b) Solution heat-treated alloy as received from the manufacturer.

Matthews, who studied the effects of thermal aging on the Charpy impact energy of Hastelloy S and Hastelloy C-4 over a temperature range of 800°F (427°C) to 1600°F (871°C). Matthews' data show that Hastelloy S suffered a maximum loss of impact energy when aged at 1400°F (760°C), while Hastelloy C-4 exhibited a maximum loss when aged at 1000°F (538°C) and 1400°F (760°C), with specimens aged at 1200°F (649°C) exhibiting higher impact energies. The differences between the PNL and Cabot data are more obvious in Figure 8, in which impact energy is plotted as a function of aging temperature. The Cabot data show that both alloys suffer a maximum loss of impact energy at about 760°C, whereas the PNL data indicate a much smaller effect for specimens aged at 700°C and higher. Reasons for the differences are not readily apparent. It is possible that the differences are related to specimen size, but this seems unlikely. It is also possible that minor differences in the compositions of the alloys used could account for the variations.

FIGURE 5. The Room-Temperature Charpy Impact Energy of Hastelloy S Specimens Heated in Air or Vacuum

5.3 EFFECTS OF LONG-TERM OXIDATION

The design specifications for the $^{90}\text{SrF}_2$ heat source requires that the outer capsule must be sufficiently resistant to oxidation to withstand 10 years of operation in air at temperatures up to 800°C without suffering a significant degradation in structural strength. This makes it necessary to accurately estimate the oxidation that Hastelloy S and Hastelloy C-4 would suffer in 10 years and the effect the oxidation would have on the capsule.

All of the data show that oxidation of Hastelloy S and Hastelloy C-4 at 600° to 800°C follows parabolic rate relationships for exposures up to 5000 h. Longer exposures lead to

FIGURE 6. The Room-Temperature Charpy Impact Energy of Hastelloy C-4 Specimens Heated in Air or Vacuum

negative deviations from the parabolic rate relationships. This means that conservative estimates of long-term oxidation of Hastelloy S and Hastelloy C-4 can be made using the parabolic rate equations given in Section 3.0. Such estimates show that oxidation of Hastelloy S in air for 10 years at 600°C to 800°C would amount to weight gains of only 0.4 to 2.3 mg/cm², while Hastelloy C-4 would suffer weight gains of 1.4 to 2.7 mg/cm² under the same conditions.

It is more difficult to estimate the subsurface attack that would result from long-term oxidation of the two alloys. The most conservative estimate would be to assume a linear

FIGURE 7. Effect of Thermal Aging on the Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4--Full-Size Specimens (Matthews 1976)

extrapolation of the data given in Tables 1 and 4. When this is done the results shown in Figures 9 and 10 are obtained. The one unusual feature is that long-term oxidation of Hastelloy S at 700°C would produce less subsurface attack than when the alloy is oxidized at 600°C. This is probably due to the differences in alloy microstructure at the two temperatures.

The data presented in Figures 9 and 10 show that when Hastelloy S and Hastelloy C-4 are oxidized at 800°C for 10 years the depth of metal affected by the oxidation reactions would be 327 and 332 μm , respectively. For a heat-source capsule having a wall thickness of 0.500 in. and an outer diameter of 3.375 in. these levels of attack would affect about 3% of

FIGURE 8. Effect of Aging Temperature on the Room-Temperature Charpy Impact Energy of Hastelloy S and Hastelloy C-4

the capsule's cross-sectional area. Results of the earlier study showed that this level of attack would have no effect on the tensile properties of the capsule. It is more difficult to estimate the effects on the impact strength of the capsule. Oxidation of the impact specimens at 800°C for 10,000 h affected the metal to a depth corresponding to greater than 5% of the cross-sectional area of the specimens without affecting their impact energy significantly. Therefore, it appears likely that attack affecting only 3% of the capsule cross section would not affect its impact strength. Because of the complex relationships between specimen size and Charpy impact energy, however, it cannot be stated with any degree of certainty that the comparison between the test specimens and capsules are valid.

FIGURE 9. Estimates of the Depth of Metal Affected When Hastelloy C-4 is Oxidized in Air at 600° to 800°C

FIGURE 10. Estimates of the Depth of Metal Affected When Hastelloy S is Oxidized in Air at 600° to 800°C

6.0 CONCLUSIONS

The oxidation of Hastelloy S and Hastelloy C-4 in air at 600⁰ to 800⁰C is very slow, and both alloys form adherent oxide layers that serve to protect the underlying metal. Oxidation of the two alloys adheres to parabolic rate relationships for exposures up to 5000 h. Larger exposures lead to negative deviations from the parabolic rate relationships. Therefore, the parabolic rate equations developed from the test data can be used to make conservative estimates of the long-term oxidation of Hastelloy S and Hastelloy C-4 in air at 600⁰ to 800⁰C.

Subsurface attack of Hastelloy S and Hastelloy C-4 due to oxidation was greater than expected, considering the slow oxidation rates of the two alloys at 600⁰ to 800⁰C. Estimates of subsurface attack, determined from micrographs of the oxidized specimens, showed erratic results and it was impossible to assign any type of rate equation to the subsurface attack. A conservative estimate of long-term effects can be made using a linear extrapolation of the test results.

There were no significant differences between the room-temperature Charpy impact energy of Hastelloy S and Hastelloy C-4 specimens oxidized in air at 600⁰ to 800⁰C and control specimens heated in vacuum. Even though subsurface attack of the oxidized specimens affected up to 5.7% of the cross-sectional area of the specimens, their Charpy impact energy was not affected. Extrapolation of the oxidation data to long-exposure times shows that subsurface attack of the heat-source outer capsule after 10 years at 800⁰C would effect only about 3% of the capsule's cross-sectional area. Therefore, it appears likely that the impact strength of the capsule would be unaffected by the subsurface attack resulting from oxidation.

REFERENCES

- Anon. 1978. Annual Book of ASTM Standards - Part 10. American Society for Testing and Materials.
- Fullam, H. T. 1980. Air Oxidation and Seawater Corrosion of Hastelloy S and Hastelloy C-4. PNL-3344, Pacific Northwest Laboratory, Richland, Washington.
- Matthews, S. J. 1976. Thermal Stability of Solid Solution Strengthened High Performance Alloys. Report No. 8979, Stellite Division - Cabot Corp., Kokomo, Indiana
- Simonen, F. A. and R. J. Shippel, Jr. 1980. Collapse of Experimental Capsules Under External Pressure. PNL-3165, Pacific Northwest Laboratory, Richland, Washington.
- Simonen, F. A., R. J. Shippel and D. G. Atteridge. 1980. Stress Analysis and Testing of the Outer Capsule Design for the Strontium Heat Source Development Program. PNL-3165, Pacific Northwest Laboratory, Richland, Washington.

ACKNOWLEDGMENTS

A number of people contributed to the work presented in this report. The experimental activities were performed by R. J. Elovich, while impact testing of the CVN specimens was carried out by G. B. Dudder. Metallographic examination of the test specimens was provided by R. H. Beauchamp and other members of the Optical Metallography group in the PNL Materials Department. The report was edited by M. H. Henry.

H. H. Van Tuyl was the program manager and overall program guidance was provided by W. C. Remini of DOE's Advanced Nuclear Systems and Projects Division.

•

•

•

•

•

•

•

•

DISTRIBUTION

<u>No. of Copies</u>		<u>No. of Copies</u>	
	<u>OFFSITE</u>		D. C. Davis, Jr. DOE Oak Ridge Operations Office P.O. Box E Oak Ridge, TN 37830
	A. A. Churm DOE Patent Division 9800 S. Cass Avenue Argonne, IL 60439		W. T. Goldston DOE Savannah River Operations Office P.O. Box A Aiken, SC 29801
	N. Goldenberg DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545	27	DOE Technical Information Center
	G. L. Bennett DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		L. J. Jardine Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439
	T. J. Holleman DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		W. R. Pardue Battelle Columbus Laboratories 505 King Avenue Columbus, OH 43201
	A. P. Litman DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		R. T. Huntoon E. I. duPont deNemours and Company Savannah River Laboratory Aiken, SC 29801
	J. J. Lombardo DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		E. H. Cooke-Yarborough Electronics and Applied Physics Division Building 347.3, AERE Harwell Oxfordshire OX11 0RA GREAT BRITAIN
3	W. C. Remini DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		H. C. Carney General Atomic Company P.O. Box 81601 San Diego, CA 92138
	B. J. Rock DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		S. E. Bronisz Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87544
	N. R. Thielke DOE Advanced Nuclear Systems and Projects Division Washington, DC 20545		R. A. Kent Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87544
	J. M. Maddox DOE E201 Washington, DC 20545		R. N. R. Mulford Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87544
	C. A. Cooley DOE Waste Management Division Washington, DC 20545		

No. of
Copies

W. T. Cave
Monsanto Research Corporation
Mount Laboratory (DOE)
Nuclear Operations
P.O. Box 32
Miamisburg, OH 45342

R. Dewitt
Monsanto Research Corporation
Mount Laboratory (DOE)
Nuclear Operations
P.O. Box 32
Miamisburg, OH 45342

Department of the Army
Headquarters, U.S. Army
Facilities Engineering Support Agency
Ford Belvoir, VA 22060
H. H. Musselman, Tech. Dir.

Officer in Charge
Lt. J. H. Vogt
Naval Nuclear Power Unit
Code 70
Port Hueneme, CA 93043

H. V. Weiss
Code 631
Naval Ocean Systems Center
San Diego, CA 92152

2 A. A. Arcuni
Naval Facilities Engineering Command
Office of Special Assistant -
Nuclear Programs (04N)
200 Stovall Street
Alexandria, VA 22332

K. W. Haff
Oak Ridge National Laboratory
Oak Ridge, TN 37830

J. Hammond
Oak Ridge National Laboratory
Oak Ridge, TN 37830

J. R. Keiser
Oak Ridge National Laboratory
Oak Ridge, TN 37830

E. Lamb
Oak Ridge National Laboratory
Oak Ridge, TN 37830

A. C. Schaffhauser
Oak Ridge National Laboratory
Oak Ridge, TN 37830

No. of
Copies

P. Dick
Teledyne Energy Systems
110 W. Timonium Road
Timonium, MD 21093

R. Hannah
Teledyne Energy Systems
110 W. Timonium Road
Timonium, MD 21093

W. A. McDonald
Teledyne Energy Systems
110 W. Timonium Road
Timonium, MD 21093

P. Vogelberger
Teledyne Energy Systems
110 W. Timonium Road
Timonium, MD 21093

C. C. Silverstein
Westinghouse Astronuclear Laboratory
P.O. Box 10864
Pittsburgh, PA 15236

ONSITE

4 DOE Richland Operations

D. Bogon
R. E. Gerton
H. A. House
H. E. Ransom

8 Rockwell Hanford Operations

L. I. Brecke
H. H. Hopkins
J. D. Kaser
E. J. Kosiancic
T. H. May
D. Ramey
J. P. Sloughter
C. R. Stroup

22 Pacific Northwest Laboratory

D. G. Atteridge
S. D. Dahlgren
H. T. Fullam (3)
M. H. Henry (2)
G. B. Long
R. E. Nightingale
N. J. Olson
L. D. Perrigo
A. M. Platt
W. E. Sande
F. A. Simonen
H. H. Van Tuyl
Technical Files (5)
Publishing Coordination EI (2)