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HIGH-TEMPERATURE IRRADIATION OF METALS
AND GRAPHITE IN FLOWING HELIUM

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As part of the coolant-core evaluation studies in an early phase of the Maritime Gas-Cooled Reactor (MGCR) program, nickel, K-Monel, niobium-1 w/o zirconium, and graphite were irradiated in a convective flow of helium. A capsule of novel design was used to study the corrosion of the metals at 1500 F and 960 F in a 243-hr BRR experiment. Four helium-filled quartz tori, containing the specimens, were encapsulated in a stainless steel capsule. A convective flow of helium was maintained in the closed tori by heating one leg of each torus to 1500 F and the other at 960 F. Zirconium foil was placed in two of the tori to getter gaseous impurities.

No attack of the nickel and niobium-1 w/o zirconium was observed at either temperature. Metallographic examination did show a 1 to 2.5-mil attack of the K-Monel at 1500 F in a torus containing no getter.

INTRODUCTION

The behavior of metals in impure helium is a well-recognized problem area in high-temperature graphite-moderated helium-cooled reactors. Gaseous impurities contained in the initial helium charge and those released by graphite outgassing may oxidize and carburize core metals and promote carbon transport. The complex spectrum of impurities in the helium is temperature dependent, consisting of hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide, water vapor, and minor amounts of hydrocarbons. The effect of radiation has not been studied. Short radiation exposures are expected to influence chiefly the composition of the coolant impurities. Longer irradiations are probably necessary before graphite outgassing is enhanced, and certainly before atomic displacements in metals influence the processes controlling the rate of growth of metal oxides and carbides at the metal surfaces.

A study of the compatibility between impure helium and core metals was initiated in an early phase of General Atomic's program on the Maritime Gas-Cooled Reactor (MGCR). In assistance to General Atomic, Battelle planned to carry out a series of BRR capsule irradiations in support of the out-of-pile studies conducted by General Atomic. A novel capsule was constructed for this program. Capsule performance was very good, clearly demonstrating that capsules can meet the demands of complex irradiation experiments.

The Battelle irradiation program was terminated after the first capsule experiment was completed. This report summarizes the design, construction, and operation of the capsule and presents the postirradiation results.

EXPERIMENTAL PROGRAM

Objectives

Originally, several capsules were to be irradiated in this program. The objective of the program was to (1) design a capsule suitable for the study of oxidation and carburization of selected metals in helium circulated over unclad graphite and (2) use this capsule to investigate the effects of temperature, helium impurity composition, radiation exposure, and graphite preirradiation history on oxidation and carburization. The effects of these variables were to be evaluated chiefly by metallographic examination of the specimens. Mass spectrometric analysis of impurities in the capsule helium were planned in order to supply supporting data for the interpretation of the metallographic results. Only one capsule was irradiated in the program, and the purpose of this capsule was to explore one set of variables. This capsule operated at specimen temperatures of 960 and 1500 F.

In the early phase of the program the objective was to design a static irradiation capsule which would allow helium to circulate over metal specimens and graphite in a closed geometry at high temperature. The chosen design utilizes a thermal gradient in the capsule to promote a convective flow of helium. This capsule design philosophy fulfills two important purposes: (1) several features characteristic of a flowing coolant in a gas-cooled reactor are simulated qualitatively, and (2) capsule capabilities are extended into research areas presently occupied entirely by loop programs.

Irradiation Capsule

The capsule consists of four elongated quartz tori in an outer stainless steel capsule shell. A thermal barrier, or baffle, along the center line of the capsule divides the capsule into two compartments. Electrical heaters maintain a temperature of 1500 F in one compartment and 950 F in the other compartment. One leg of each torus is in the hot compartment, and one is in the cool compartment. The specimens are located in the legs of the helium-filled tori. The capsule design is shown in Figure 1.

Three different metals were selected for study in this capsule. With four tori it is possible to study several aspects of the problem in one capsule, examining (1) the behavior of the helium-metal-graphite system, (2) the effect of a getter on the impurity composition of the helium, and (3) the behavior of the helium-graphite system in the absence of metals. The torus design is shown in Figure 2, and the assembled tori are shown in Figure 3. Two of the tori contain zirconium foil to getter impurities in the helium. All four tori contain graphite specimens in both legs. Tori specimens are listed in Table 1.

FIGURE 1. IRRADIATION CAPSULE

B-33142

FIGURE 2. QUARTZ TORUS

FIGURE 3. ASSEMBLED QUARTZ TORI

N57409

TABLE 1. TORI SPECIMENS

Torus	Specimen		Zirconium Getter	
	Leg 1 (960 F)	Leg 2 (1500 F)	Leg 1 (960 F)	Leg 2 (1500 F)
1	Graphite	Graphite	No	No
2	Graphite	Graphite	No	Yes
3	Graphite, K-Monel, nickel, and Nb-1 w/o Zr	Graphite, K-Monel, nickel, and Nb-1 w/o Zr	No	No
4	Graphite, K-Monel, nickel, and Nb-1 w/o Zr	Graphite, K-Monel, nickel, and Nb-1 w/o Zr	Yes	No

Torus Design

Clear fused quartz was selected for the torus material (Figure 2) because of its relative inertness and its good high-temperature strength. Initially, long cylindrical containers were considered, but calculations of the convective gas flow in this latter geometry indicated that gas circulation was very poor. Bench tests with a mock-up of the torus showed that the time required for a complete cycle of the gas in the torus was less than 1 min.

A quartz support rod runs axially along each leg of the torus and supports the cylindrical graphite specimens and the washer-shaped metal specimens. Quartz spacers separate the metal specimens.

The torus is fabricated with one end of each leg open, and the support rod is attached at the closed end of the leg. After weighing, the specimens are loaded into the torus, and the latter is preflushed with helium. A taper joint with a break seal is sealed to one of the legs, and the free ends of the support rods are sealed to the torus wall. The torus is evacuated through the open leg, filled with helium (10 in. of mercury), and sealed. Commercial 99.78 mole per cent helium, containing small amounts of CO₂, oxygen, nitrogen, and water vapor, is used without further purification.

The tori rest on cutouts in the baffle. Strands of quartz fibers are used to secure the tori to the baffle. Quartz-wool padding minimizes mechanical shock. Thermocouple wells (Figure 1) are tied to the tori with quartz fibers.

Capsule Design

Two half-cylinder heaters, one in each compartment, supply the desired temperature gradient in the capsule (Figure 1). Electrical heater units are brazed to axial grooves in the outside surface of the heater shells. Each heater unit consists of a 50-in. length of 24-gage Kanthal heater wire, butt welded at each end to a 24-in. length of nickel lead wire. Both the heater and lead wires are insulated in compacted MgO powder, and contained in a 1/16-in.-OD stainless steel sheath. Each heater unit is nominally rated at 1000 w. Seven heater units are brazed on the center 14 in. of one shell, and three on the other shell. The two shells are held in a cylindrical geometry by brazing both to a stainless steel header at one end. The other end of this geometry is loosely held by a ring. This ring allows axial slipping of one shell past the other during differential thermal expansion. The sheathed nickel heater leads pass through drilled holes in the header, and are brazed to the latter.

The interior of the capsule is divided axially into two compartments by the metal baffle. This baffle is made of 1/16-in. -thick polished nickel sheet with two 0.010-in. -thick polished nickel sheets attached on both sides. A 1/16-in. gas space separates adjacent sheets. This baffle provides the necessary thermal barrier between the two capsule compartments and supports the tori.

All thermocouples are located outside the tori. Two thermocouples, one in each capsule compartment, are used to measure the "average" tori temperatures. Each thermocouple is placed in a stainless steel thermocouple well tied to the tori. This well is blackened and should have approximately the same emissivity as the graphite specimens. The wells and graphite specimens are about the same distance away from the shell heaters. Accordingly, the graphite and wells see a similar thermal-radiation environment.

An additional six thermocouples are located between the heater shells and the outer capsule shell.

The furnace and tori assembly is encapsulated in a stainless steel cylinder which is welded to the top header and closed at the bottom by a weld to a bottom plug. An extension shown on the bottom plug is used to hold the capsule in the hot-cell capsule-opening device. An aluminum core-plate plug is attached to a threaded stud on the bottom of the capsule to position the capsule in the reactor core. The heater and thermocouple leads extend from 1 to 3 ft up the lead tube. Each heater lead is connected to a 14-gage glass-insulated copper conductor. The thermocouple leads are connected to glass-insulated Chromel-Alumel duplex conductors. All of the leadout conductors extend through an epoxy-resin seal at the top of the 25-ft lead tube.

Capsule Assembly

The furnace and leads are brazed to the top of the header. After the outer capsule shell is slipped over the furnace and welded to the header, the baffle, loaded with tori, is placed in the furnace through the open end. The baffle rides in two slots on the inside of the furnace, and rests on a Lavite plate on the bottom of the capsule. The partially assembled capsule is evacuated and filled with helium to atmospheric pressure in a dry box. The bottom plug is welded in a helium atmosphere. Capsule assembly is completed by welding the upper chamber to the header, making connections to the leadout conductors, and attaching the lead tube.

Specimen Preparation

The cylindrical graphite specimens were machined from an as-received bar of reactor-grade AGOT graphite. Prior to insertion in the tori the specimens were degassed in vacuum at 1000 F for 48 hr and stored in a helium atmosphere.

Nickel, K-Monel, and niobium-1 w/o zirconium specimens, in the shape of thin washers, were cut from as-received cold-rolled sheet stock. The specimens were degreased, but not polished or etched, prior to loading the tori.

Capsule Operation

The capsule was irradiated in a core position of the Battelle Research Reactor. Based on previous dosimetry experience in this core position, the radiation intensities were estimated to be:

Total fast-neutron flux (fission spectrum)	$2 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$
Thermal-neutron flux	$1 \times 10^{13} \text{ n}/(\text{cm}^2)(\text{sec})$
Absorbed dose rate in graphite (fast neutron plus gamma)	$1.5 \times 10^8 \text{ rads per hr}$
Ratio of fast-neutron dose rate to gamma dose rate	0.5

The two thermocouples adjacent to the tori were used to control the tori temperatures. Each controlled the power input to a shell heater. The control system consisted of a controller, a magnetic amplifier, a saturable reactor, and a recorder. The output of all thermocouples was continuously recorded during irradiation.

Capsule insertion in the BRR occurred during a scheduled shutdown. During the shutdown, electrical power was applied to the heaters to determine the temperature performance of the capsule in the absence of gamma heating. Temperatures of 1500 and 750 F were achieved in the hot and cool legs of the tori with power inputs of 5 kw and 0.4 kw into the respective heaters. The capsule was in-pile for one BRR cycle (288 hr). Reactor scrams reduced the total irradiation time to 243 hr. Shortly after the BRR reached full operating power of 2 megawatts, heater power was adjusted to give hot- and cool-leg temperatures of 1500 and 960 F. It was not necessary to use the heater in the cool compartment to achieve the 960 F temperature.

Capsule performance was very good. During irradiation, the tori temperatures did not vary more than 10 F about the operating temperatures listed above.

Postirradiation Results

Postirradiation examination included metallography and weight and microhardness measurements on the metal specimens. The graphite specimens were weighed and examined at low magnification, but metallographic examination of the graphite specimens was not attempted. Only small changes in the graphite microstructure were expected, and these would be difficult to detect. It was not possible to analyze the tori helium. During removal of the baffle from the capsule, the tori broke into several large pieces.

There was no evidence of carbon deposition on the few large pieces of quartz examined. One of the zirconium getters (Torus 2) was not recovered. This foil may have become lodged in the capsule when the tori broke.

Graphite Specimens

All graphite specimens were intact. As expected, examination at low magnification revealed no gross changes in surface appearance between these specimens and an unirradiated control. Weight-change data on these nominal 5-g specimens are reported in Table 2. With the exception of the 960 F specimen in Torus 1, all specimens lost weight. A getter appears to increase the weight loss. Small weight changes are difficult to measure accurately and the difference among the values may not be real. Weight losses of 1 mg are frequently observed in long laboratory heat treatments of previously degassed, 5-g specimens of graphite in a helium atmosphere.

TABLE 2. POSTIRRADIATION WEIGHT MEASUREMENTS

Torus	Specimen Weight Change, mg									
	Graphite		Nickel		K-Monel		Nb-1 w/o Zr		Getter	
	960 F	1500 F	960 F	1500 F	960 F	1500 F	960 F	1500 F	960 F	1500 F
1	+0.2	-1.1	--	--	--	--	--	--	--	--
2	-1.2	-1.8	--	--	--	--	--	--	--	(a)
3	-0.9	-1.0	-8.2	+0.2	+0.5	+0.2	-4.4	+7.4	--	--
4	-1.4	-1.3	-9.5	+0.3	+0.1	+0.2	+0.5	+0.9	+1	--

(a) Not recovered.

Metal Specimens

Visual examination of the tori metals revealed only slight discoloration.

The nominal 0.2-g tori metals were weighed, rough ground, and finished with 600-grit SiC paper. A Syntron vibratory polisher was used to polish the specimens with slurries of 1- μ alumina, Linde A, and Linde B on Microcloths.

Concentrated nitric acid was used to etch the nickel and K-Monel. The etch for the niobium-1 w/o zirconium alloy consisted of a mixture of 50 ml of lactic acid, 30 ml of nitric acid, and 10 ml of hydrogen fluoride. An unirradiated control specimen of each metal was prepared by the same techniques.

Microhardness measurements were made with a Tukon tester using a 200-g load and a Knoop-type indenter.

Photomicrographs (100X) of the low-temperature metal specimens and control specimens are shown in Figure 4. There was no evidence of oxidation or carburization of the nickel, K-Monel, or niobium-1 w/o zirconium at 960 F. Several photomicrographs at 500X (not shown) confirmed this observation. Weight changes were observed in all 960 F specimens, but these changes do not correlate with the results of the metallographic examination.

In contrast to the 960 F specimens, all the 1500 F metal specimens showed weight gains (Table 2). Photomicrographs of the 1500 F specimens are shown in Figure 5. At this temperature some grain growth and recrystallization occurred through the specimens of nickel and K-Monel. The K-Monel specimen in Torus 3 (no getter) showed attack and segregation at the surfaces. The depth of attack was 1 to 2.5 mils. In

100X

HC2983

Control

100X

HC2985

Torus No. 3

100X

HC2987

Torus No. 4

a. Nickel Specimens

100X

HC2968

Control

100X

HC2970

Torus No. 3

100X

HC2972

Torus No. 4

b. K-Monel Specimens

100X

HC2953

Control

100X

HC2958

Torus No. 3

100X

HC2965

Torus No. 4

c. Niobium-1 w/o Zirconium Specimens

FIGURE 4. PHOTOMICROGRAPHS OF TORI SPECIMENS EXPOSED AT 960 F

No oxidation or carburization is evident on any specimen.

a. Nickel Specimens

b. K-Monel Specimens

c. Niobium-1 w/o Zirconium Specimens

FIGURE 5. PHOTOMICROGRAPHS OF TORI SPECIMENS EXPOSED AT 1500 F

Some grain growth and recrystallization are evident in the photomicrographs of the irradiated nickel and K-Monel specimens. Notice the surface attack in the K-Monel specimen exposed in Torus 3, in which no zirconium getter was present. The niobium-1 w/o zirconium specimens were not attacked; the origin of the dark zone (Torus No. 3) is unknown.

100X

HC2964

500X

HC2989

FIGURE 6. PHOTOMICROGRAPHS OF NICKEL SPECIMEN EXPOSED AT 1500 F IN TORUS 3
WITHOUT A ZIRCONIUM GETTER

FIGURE 7. PHOTOMICROGRAPHS OF K-MONEL SPECIMEN EXPOSED AT 1500 F IN TORUS 3 WITHOUT A ZIRCONIUM GETTER

Torus 4, which contained getter, there was no evidence of attack in the K-Monel specimen. The metallographic results on the two K-Monel specimens at 1500 F did not correlate with the weight changes observed in these two specimens.

Very little, if any, attack was observed in the nickel specimens at 1500 F. Figures 6 and 7 show photomicrographs of the nickel and K-Monel specimens at 500X.

There was no evidence of attack in the niobium-1 w/o zirconium specimens at 1500 F. The cause of the dark zone (Torus No. 3) visible in Figure 5 is unknown. Repolishing and re-etching did not remove this zone. The zone does not overlap the specimen surfaces and is not believed to influence gas-metal reactions at the surfaces.

All the 1500 F specimens were repolished, and microhardness measurements were made across the specimens. These microhardness scans are summarized in Table 3. The specimens were then re-etched, and additional photomicrographs were prepared. These photomicrographs (not shown) confirmed the above results.

TABLE 3. MICROHARDNESS MEASUREMENTS ON 1500-F METAL SPECIMENS

Specimen	Torus	Knoop Hardness ^(a) Readings								
Nickel	3	73	68.2	84.3	96.8	80.5	74.1	94.8		
	4	101	98.5	87.4	80.5	91.9	93.1	95.7		
K-Monel	3	65.4	99.1	97.3	95.1	88.8	93.1	98.5	90.8	90.8
	4	103	117	113	107	109	108	127	127	
Nb-1 w/o Zr	3	347	408	408	394	394	394	381	408	399
	4	203	251	171	162	163	182	171	235	

(a) 200-g load.

Microhardness determinations were not made on unirradiated specimens. With the exception of the K-Monel specimen in Torus 3, the hardness scan started and ended two indenter widths (2 mils) away from the metal surfaces. The lowest value for this latter specimen was for the interface between the bulk of the specimen and the surface segregation. This specimen showed the greatest attack (Figure 5) but there was no significant change in hardness across the scan. There was some evidence of a downward trend in hardness values as the midplane of the nickel specimen in Torus 4 was approached. No significant change in hardness occurred within any of the remaining five scans, as shown in Table 3. Comparison of the two scans for each metal revealed the difference between the Torus 3 and Torus 4 specimens. The hardness of the niobium-1 w/o zirconium specimen in Torus 3 was significantly higher than the hardness of the Torus 4 specimen.

CONCLUSIONS

Nickel, K-Monel, niobium-1 w/o zirconium, and graphite were irradiated for 243 hr in a convective flow of impure helium as part of an early study of oxidation, carburization, and carbon transport for the MGCR. In this BRR experiment specimens were

heated at 960 and 1500 F in four helium-filled tori. Two of the tori contained zirconium foils to getter gaseous impurities. Good capsule performance was achieved in this initial experiment, demonstrating that the novel capsule design is well suited to the study of these coolant-core materials problems.

None of the metals was attacked at 960 F. At 1500 F, K-Monel (no getter) showed 1 to 2.5 mils of attack, consisting of grain-boundary penetration and segregation at the surface. Nickel was slightly attacked at the higher temperature, but the depth of attack was not well defined. The niobium-1 w/o zirconium was not attacked at 1500 F.

The results are consistent with the general behavior of the graphite specimens and the getter. Graphite showed weight losses in each torus, contaminating the tori helium with gaseous impurities. Only one of the K-Monel specimens exposed at 1500 F was attacked, and this specimen was in a torus containing no getter. Accordingly, the corrosion of K-Monel at 1500 F is more sensitive to the concentration of impurities in the helium than nickel and niobium-1 w/o zirconium. None of the metals was attacked at 960 F, and, presumably, the rate of attack over a 243-hr period at this temperature is not very sensitive to the concentration of impurities in the helium.

NEM:DJH:WSD:WHG/mmk