In-pile Hydrothermal Corrosion Evaluation of Coated SiC Ceramics and Composites

Nuclear Technology Research and Development

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SUMMARY

Hydrothermal corrosion accelerated by water radiolysis during normal operation is among the most critical technical feasibility issues remaining for silicon carbide (SiC) composite-based cladding that could provide enhanced accident-tolerance fuel technology for light water reactors. An integrated in-pile test was developed and performed to determine the synergistic effects of neutron irradiation, radiolysis, and pressurized water flow, all of which are relevant to a typical pressurized water reactor (PWR). The test specimens were chosen to cover a range of SiC materials and a variety of potential options for environmental barrier coatings. This document provides a summary of the irradiation vehicle design, operations of the experiment, and the specimen loading into the irradiation vehicle.

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ACRONYMS

ATF	accident tolerant fuel
AFC	Advanced Fuels Campaign
COATI	ORNL Hybrid Composites Loop ATF Irradiation
DOE-NE	US Department of Energy Office of Nuclear Energy
EBC	environmental barrier coatings
LWR	light water reactor
MIT	Massachusetts Institute of Technology
MITR	Massachusetts Institute of Technology Nuclear Reactor Laboratory’s Research Reactor
NTRD	Nuclear Technology Research and Development
ORNL	Oak Ridge National Laboratory
PWR	pressurized water reactor
SiC/SiC	silicon carbide continuous fiber-reinforced silicon carbide matrix
SiC	silicon carbide (SiC)

ACKNOWLEDGMENTS

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1. OBJECTIVES

Silicon carbide (SiC) continuous fiber-reinforced SiC matrix (SiC/SiC) composite-based fuel cladding is considered a leading candidate among the enhanced accident-tolerant fuel (ATF) technologies for light water reactors for a number of reasons including exceptional high temperature stability and slow kinetics for steam oxidation in beyond-design basis accident conditions [1–3]. However, hydrothermal corrosion during normal operation is among the most critical technical feasibility issues remaining for SiC-based fuel cladding for light water reactor (LWR) applications [4,5]. This is particularly the case since water radiolysis is now known to accelerate the hydrothermal corrosion of SiC at LWR-relevant temperatures [5,6]. To address this issue, integrated in-pile tests must be conducted that combine the key elements of the normal operating environment for LWR fuels: mixed thermal and fast spectrum neutrons, flowing water of relevant chemistry at a relevant temperature, and ionizing radiation capable of radiolysis of water. The objective of the work reported in this document is to design, implement, and perform an experiment that allows exposure of test specimens in such an integrated environment.

2. INTRODUCTION

This report details the design, development, and operation of an in-pile hydrothermal corrosion experiment that is being conducted in support of the Light Water Reactor (LWR) Core Materials, Advanced Fuels Campaign (AFC), which is funded by the Nuclear Technology Research and Development (NTRD) Program of the Office of Nuclear Energy, US Department of Energy. In this activity, irradiation vehicles were designed to allow exposure of a large number of test specimens to both neutrons and ionizing radiation in a water loop that simulates coolant conditions of a pressurized water reactor (PWR) (relevant water chemistry and temperature) in the Massachusetts Institute of Technology (MIT) Nuclear Reactor Laboratory's Research Reactor (MITR). Researchers at Oak Ridge National Laboratory (ORNL) designed the specimen matrix to allow evaluation of bulk silicon carbide (SiC) (varied quality), continuous SiC fiber-reinforced SiC matrix (SiC/SiC) composites, and SiC ceramics and composites with various environmental barrier coatings (EBC). This document contains a brief description of the MIT Research Reactor, a description of the capsule design and specimen test matrix, and irradiation results. Complete records of irradiation vehicle fabrication and experimental operation are maintained at the MIT Nuclear Reactor Laboratory [7].

3. IRRADIATION EXPERIMENT DESIGN

3.1 Description of the MIT Research Reactor

The MIT Reactor (MITR) is a light-water cooled and moderated research reactor with in-core experimental facilities. The core consists of finned plate-type fuel elements which currently use highly enriched ^{235}U fuel with a core power density averaging 70kW per liter. Heavy water surrounding the core reflects neutrons providing researchers with a maximum fast and thermal neutron flux of 1.2×10^{14} and 6×10^{13} neutrons/cm^2-s, respectively [7].

3.2 Summary of Capsule Design

Separate irradiation vehicles were designed to allow exposure to PWR loop water in a) an in-core position where specimens are exposed to high energy neutrons and water radiolysis products, b) an above-core position where specimens are exposed to water radiolysis products without significant neutron damage, and c) an out-of-core position without water radiolysis or neutron damage. The ORNL Hybrid Composites Loop ATF Irradiation was designated as "COATI" by the MITR. Table 1 summarizes the irradiation vehicles. The computer-aided design illustrations of the individual vehicles are shown in Figure 1 and the full length loop experiment is shown in Figure 2. Note that Modules 3, 6, and 9 are identical, and so are Modules 4, 7, and 10.

Table 1 - Summary of irradiation vehicles for this experiment

Module #	Position	Alias	Specimen Type
3	In-core	In-core ORNL 1	Tubes
4	In-core	In-core ORNL 2	Coupons
6	Above-core	Above-core ORNL 1	Tubes
7	Above-core	Above-core ORNL 2	Coupons
9	Out-of-core	Out-of-core ORNL 1	Tubes
10	Out-of-core	Out-of-core ORNL 2	Coupons

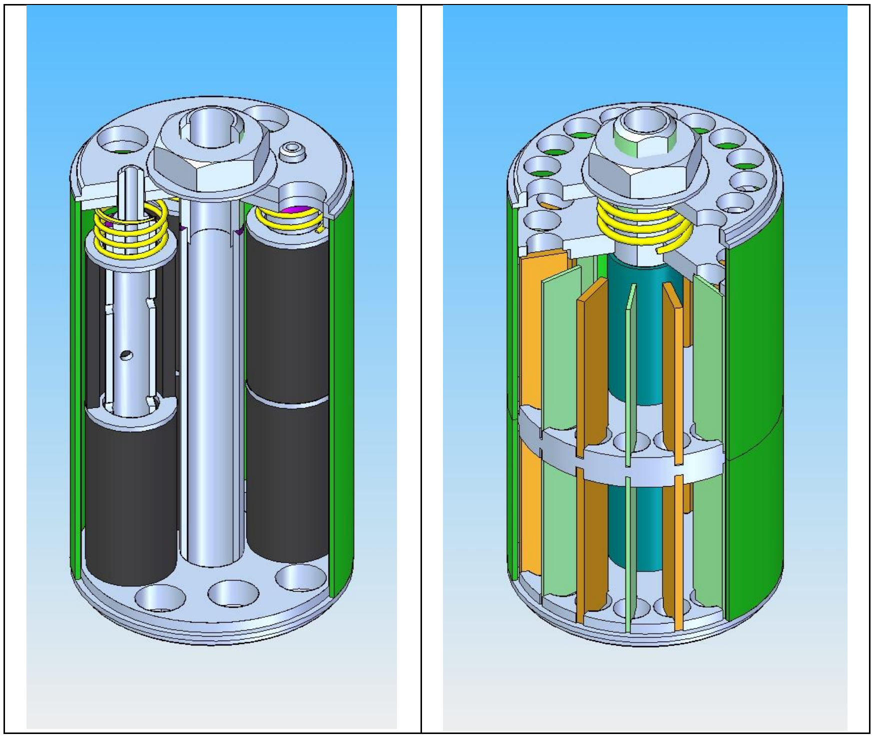

Figure 1 - Illustration of irradiation vehicles: Modules 3, 6, and 9 for tubular specimens (left) and Modules 4, 7, and 10 for coupon specimens (right).

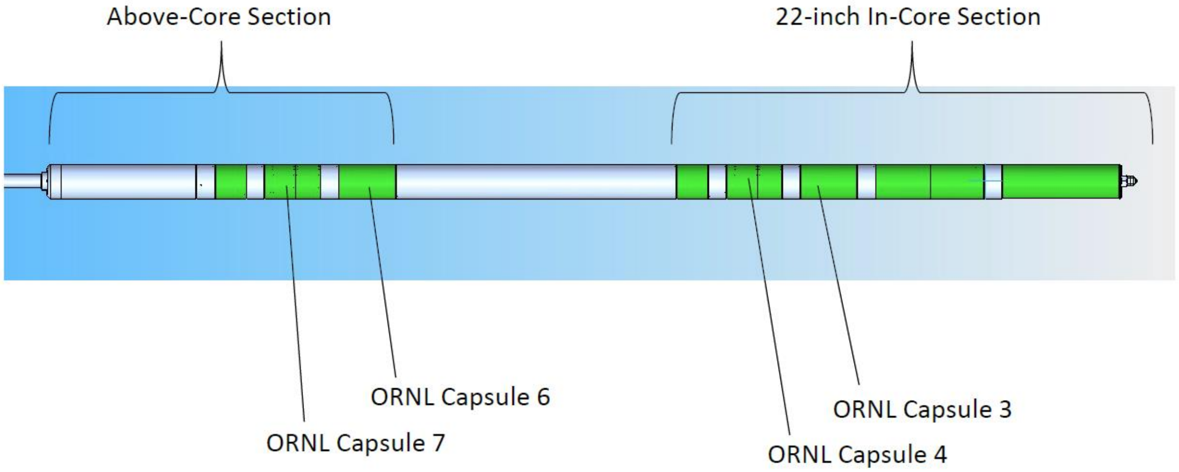

Figure 2 - COATI in- and above-core capsule locations within the autoclave stack

3.3 Experiment Test Plan Materials

A detailed listing of the specimen coupon and tube materials used in this study are provided in Appendix A. The test matrix includes nearly identical specimens in the three experiment positions (in-core, above-core, and out-of-core). Table 2 summarizes the total number of specimens in each experiment location by specimen type. A total of 22 tubes and 96 coupons are being studied in the COATI experiment.

Table 2 - Specimen Summary by Location, Module and Type

Location	Module	Specimen Type	Total
Above-Core	6	Tube	8
	7	Coupon	32
Above-Core Total			40
In-Core	3	Tube	6
	4	Coupon	32
In-Core Total			38
Out-of-Core	9	Tube	8
	10	Coupon	32
Out-of-Core Total			40

4. SUMMARY OF IRRADIATION RESULTS

The COATI facility irradiation experiment operated for two cycles and was temporarily placed in dry storage between cycles. The first cycle started January 18, 2017 and ended on April 8, 2017. The second cycle started May 4, 2017 and ended on July 2, 2017. Several planned and un-planned reactor power changes occurred during these cycles and the loop was also shut down once in February due to a failing check-valve. MIT collected data on loop temperatures, pressure, flow, and reactor power throughout the experiment. Overall, the loop maintained constant temperature, pressure and flow whenever the reactor was operating. Statistics on cycles 1 and 2 are reported in Table 3. All ORNL capsules (3 and 4 in-core, 6 and 7 above-core, and 9 and 10 out-of-core) were exposed to the same temperature, pressure, and water flow. The times during which the autoclave was operating at the nominal temperature of 296°C are reported as “Hot Days.” The neutron fluences that are reported are spatially averaged over the in-core region.

Table 3 - COATI Cycle Statistics

Cycle 1 (1/18/17-4/8/17)	
Elapsed Hours	1921
Hot Days	70
Integrated Reactor Power × Operating Time (MWd)	379
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	6.77×10^{20}
Total Neutron Fluence (n/cm^2)	1.53×10^{21}

Cycle 2 (5/4/17-7/2/17)	
Elapsed Hours	1427
Hot Days	57
Integrated Reactor Power × Operating Time (MWd)	295
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	5.26×10^{20}
Total Neutron Fluence (n/cm^2)	1.19×10^{21}

The position of the ORNL COATI capsules in relation to the centerline of the core directly impacts the fast and thermal neutron flux calculated for each capsule. Capsule 3 was placed between +1 inch and +4 inches above the core centerline. Capsule 4 was placed between +5 and +8 inches above the core centerline. The calculated average neutron fluence for each capsule are reported in Table 4 based on the capsule position and the calculated neutron flux spatial gradients in the core.

Table 4 - Adjusted Neutron Fluence for ORNL Capsules

Cycle 1 (1/18/17-4/8/17)	
Capsule 3	
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	6.08×10^{20}
Total Neutron Fluence (n/cm^2)	1.41×10^{21}
Capsule 4	
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	4.70×10^{20}
Total Neutron Fluence (n/cm^2)	1.10×10^{21}

Cycle 2 (5/4/17-7/2/17)	
Capsule 3	
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	4.72×10^{20}
Total Neutron Fluence (n/cm^2)	1.09×10^{21}
Capsule 4	
Fast Neutron Fluence (Energy > 0.1 MeV) (n/cm^2)	3.64×10^{20}
Total Neutron Fluence (n/cm^2)	8.54×10^{20}

After irradiation, the experiment was moved to dry storage at the MIT hot cell where it will be disassembled.

5. FUTURE WORK

The irradiated test specimens will be examined following capsule disassembly and shipped to an appropriate post-irradiation examination facility. Examination will include visual inspection and optical microscopy for evaluating the surface appearance and coating integrity. Other examinations will include dimensional and mass measurements as well as microstructural characterization and determination of micro-mechanical properties.

6. REFERENCES

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7. APPENDIX A

Module	Location	Layer	Position	Specimen Type	Material Class	Base Material	Coating Material
3	In-Core	1	c	Tube	Coated SiC/SiC	GA HNS/CVI	PVD ZrN(1-x)
3	In-Core	1	d	Tube	Coated SiC/SiC	GA HNS/CVI	UWM Zr-Si
3	In-Core	2	e	Tube	Coated SiC/SiC	GA HNS/CVI	PVD CrN(1-x)-Cr2N
3	In-Core	2	f	Tube	SiC/SiC	GA HNS/CVI	(none)
3	In-Core	2	g	Tube	Coated SiC/SiC	GA HNS/CVI	PVD TiN
3	In-Core	2	h	Tube	FeCrAl	C36M3	(none)
4	In-Core	1	a	Coupon	Monolithic	CT HP SiC	(none)
4	In-Core	1	b	Coupon	Monolithic	CT CVD SiC HR	(none)
4	In-Core	1	c	Coupon	Monolithic	CT HP SiC	(none)
4	In-Core	1	d	Coupon	Monolithic	CT CVD SiC HR	(none)
4	In-Core	1	e	Coupon	Monolithic	CT HP SiC	(none)
4	In-Core	1	f	Coupon	Monolithic	CT CVD SiC LR	(none)
4	In-Core	1	g	Coupon	Coated SiC/SiC	HHTC SA3/CVI	PVD Cr
4	In-Core	1	h	Coupon	Monolithic	CT CVD SiC LR	(none)
4	In-Core	1	i	Coupon	Monolithic	NITE SiC-YAG	(none)
4	In-Core	1	j	Coupon	Coated SiC	R&H CVD SiC HR	PVD Cr
4	In-Core	1	k	Coupon	Coated SiC	R&H CVD SiC HR	EP Cr2Si-Ni2Si
4	In-Core	1	l	Coupon	Coated SiC	R&H CVD SiC HR	PVD CrN(1-x)-Cr2N

Module	Location	Layer	Position	Specimen Type	Material Class	Base Material	Coating Material
4	In-Core	1	m	Coupon	Coated SiC	R&H CVD SiC HR	EP PyC-Cr
4	In-Core	1	n	Coupon	Coated SiC	R&H CVD SiC HR	PVD TiN(1-x)
4	In-Core	1	o	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
4	In-Core	1	p	Coupon	Monolithic	R&H CVD SiC HR	(none)
4	In-Core	2	q	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
4	In-Core	2	r	Coupon	Monolithic	R&H CVD SiC HR	(none)
4	In-Core	2	s	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
4	In-Core	2	t	Coupon	Monolithic	Cree 6H-SiC	(none)
4	In-Core	2	u	Coupon	Coated SiC	R&H CVD SiC HR	UWM Zr-Si
4	In-Core	2	v	Coupon	Monolithic	Cr	(none)
4	In-Core	2	w	Coupon	Coated SiC	R&H CVD SiC HR	PVD ZrN(1-x)
4	In-Core	2	x	Coupon	FeCrAl	Kanthal AF	(none)
4	In-Core	2	y	Coupon	FeCrAl	C06M	(none)
4	In-Core	2	z	Coupon	FeCrAl	Kanthal AF	(none)
4	In-Core	2	aa	Coupon	FeCrAl	C06M	(none)
4	In-Core	2	ab	Coupon	Zr alloy	Zircaloy-4	(none)
4	In-Core	2	ac	Coupon	FeCrAl	C36M	(none)
4	In-Core	2	ad	Coupon	Zr alloy	Zircaloy-4	(none)
4	In-Core	2	ae	Coupon	FeCrAl	C36M	(none)
4	In-Core	2	af	Coupon	Monolithic	Cree 6H-SiC	(none)

Module	Location	Layer	Position	Specimen Type	Material Class	Base Material	Coating Material
6	Above-Core	1	a	Tube	FeCrAl	C36M3	(none)
6	Above-Core	1	b	Tube	FeCrAl	B136Y	(none)
6	Above-Core	1	c	Tube	Coated SiC/SiC	GA HNS/CVI	EP Ni-Cr
6	Above-Core	1	d	Tube	Coated SiC/SiC	GA HNS/CVI	PVD CrN(1-x)-Cr2N
6	Above-Core	2	e	Tube	Coated SiC/SiC	GA HNS/CVI	PVD TiN(1-x)
6	Above-Core	2	f	Tube	SiC/SiC	GA HNS/CVI	(none)
6	Above-Core	2	g	Tube	Coated SiC/SiC	GA HNS/CVI	PVD ZrN(1-x)
6	Above-Core	2	h	Tube	Zr alloy	Zircaloy-4	(none)
7	Above-Core	1	a	Coupon	Coated SiC	CT HP SiC	PVD CrN
7	Above-Core	1	b	Coupon	Coated SiC	R&H CVD SiC HR	PVD CrN(1-x)-Cr2N
7	Above-Core	1	c	Coupon	Coated SiC	CT HP SiC	PVD Cr2N
7	Above-Core	1	d	Coupon	Coated SiC	R&H CVD SiC HR	PVD Cr
7	Above-Core	1	e	Coupon	Monolithic	CT HP SiC	(none)
7	Above-Core	1	f	Coupon	Coated SiC	R&H CVD SiC HR	PVD TiN(1-x)
7	Above-Core	1	g	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
7	Above-Core	1	h	Coupon	Monolithic	Cree 6H-SiC	(none)
7	Above-Core	1	i	Coupon	Coated SiC	R&H CVD SiC HR	EP Cr2Si-Ni2Si
7	Above-Core	1	j	Coupon	Monolithic	CT CVD SiC LR	(none)
7	Above-Core	1	k	Coupon	Coated SiC	R&H CVD SiC HR	EP PyC-Cr
7	Above-Core	1	l	Coupon	Monolithic	CT CVD SiC LR	(none)
7	Above-Core	1	m	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr

Module	**Location**	**Layer**	**Position**	**Specimen Type**	**Material Class**	**Base Material**	**Coating Material**
7	Above-Core	1	n	Coupon	Monolithic	CT CVD SiC HR	(none)
7	Above-Core	1	o	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
7	Above-Core	1	p	Coupon	Monolithic	CT CVD SiC HR	(none)
7	Above-Core	2	q	Coupon	Coated SiC	R&H CVD SiC HR	UWM Zr-Si
7	Above-Core	2	r	Coupon	Monolithic	R&H CVD SiC HR	(none)
7	Above-Core	2	s	Coupon	Monolithic	NITE SiC-YAG	(none)
7	Above-Core	2	t	Coupon	Monolithic	R&H CVD SiC HR	(none)
7	Above-Core	2	u	Coupon	Coated SiC/SiC	HHTC SA3/CVI	PVD Cr
7	Above-Core	2	v	Coupon	Coated SiC	R&H CVD SiC	PVD Cr
7	Above-Core	2	w	Coupon	Coated SiC	R&H CVD SiC HR	PVD ZrN(1-x)
7	Above-Core	2	x	Coupon	FeCrAl	Kanthal AF	(none)
7	Above-Core	2	y	Coupon	FeCrAl	C06M	(none)
7	Above-Core	2	z	Coupon	FeCrAl	Kanthal AF	(none)
7	Above-Core	2	aa	Coupon	FeCrAl	C06M	(none)
7	Above-Core	2	ab	Coupon	Zr alloy	Zircaloy-4	(none)
7	Above-Core	2	ac	Coupon	FeCrAl	C36M	(none)
7	Above-Core	2	ad	Coupon	Zr alloy	Zircaloy-4	(none)
7	Above-Core	2	ae	Coupon	FeCrAl	C36M	(none)
7	Above-Core	2	af	Coupon	Coated SiC	R&H CVD SiC HR	PVD CrN(1-x)
9	Out-of-Core	1	a	Tube	FeCrAl	C36M3	(none)
9	Out-of-Core	1	b	Tube	FeCrAl	B136Y	(none)

Module	Location	Layer	Position	Specimen Type	Material Class	Base Material	Coating Material
9	Out-of-Core	1	c	Tube	Coated SiC/SiC	GA HNS/CVI	EP Ni-Cr
9	Out-of-Core	1	d	Tube	Coated SiC/SiC	GA HNS/CVI	PVD CrN(1-x)-Cr2N
9	Out-of-Core	2	e	Tube	Coated SiC/SiC	GA HNS/CVI	PVD TiN(1-x)
9	Out-of-Core	2	f	Tube	SiC/SiC	GA HNS/CVI	(none)
9	Out-of-Core	2	g	Tube	Coated SiC/SiC	GA HNS/CVI	PVD ZrN(1-x)
9	Out-of-Core	2	h	Tube	Zr alloy	Zircaloy-4	(none)
10	Out-of-Core	1	a	Coupon	Monolithic	CT HP SiC	(none)
10	Out-of-Core	1	b	Coupon	Coated SiC	R&H CVD SiC HR	PVD CrN(1-x)-Cr2N
10	Out-of-Core	1	c	Coupon	Coated SiC	CT HP SiC	PVD Cr2N
10	Out-of-Core	1	d	Coupon	Coated SiC	R&H CVD SiC HR	PVD Cr
10	Out-of-Core	1	e	Coupon	Monolithic	CT HP SiC	PVD TiN
10	Out-of-Core	1	f	Coupon	Coated SiC	R&H CVD SiC HR	PVD TiN(1-x)
10	Out-of-Core	1	g	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
10	Out-of-Core	1	h	Coupon	Monolithic	Cree 6H-SiC	(none)
10	Out-of-Core	1	i	Coupon	Coated SiC	R&H CVD SiC HR	EP Cr2Si-Ni2Si
10	Out-of-Core	1	j	Coupon	Monolithic	CT CVD SiC LR	(none)
10	Out-of-Core	1	k	Coupon	Coated SiC	R&H CVD SiC HR	EP PyC-Cr
10	Out-of-Core	1	l	Coupon	Monolithic	CT CVD SiC LR	(none)
10	Out-of-Core	1	m	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
10	Out-of-Core	1	n	Coupon	Monolithic	CT CVD SiC HR	(none)

Module	Location	Layer	Position	Specimen Type	Material Class	Base Material	Coating Material
10	Out-of-Core	1	o	Coupon	Coated SiC	R&H CVD SiC HR	EP Ni-Cr
10	Out-of-Core	1	p	Coupon	Monolithic	CT CVD SiC HR	(none)
10	Out-of-Core	2	q	Coupon	Coated SiC/SiC	HHTC SA3/CVI	UWM Zr-Si
10	Out-of-Core	2	r	Coupon	Monolithic	R&H CVD SiC HR	(none)
10	Out-of-Core	2	s	Coupon	Monolithic	NITE SiC-YAG	(none)
10	Out-of-Core	2	t	Coupon	Monolithic	R&H CVD SiC HR	(none)
10	Out-of-Core	2	u	Coupon	Coated SiC/SiC	HHTC SA3/CVI	PVD Cr
10	Out-of-Core	2	v	Coupon	Monolithic	Cr	(none)
10	Out-of-Core	2	w	Coupon	Coated SiC	R&H CVD SiC HR	PVD ZrN(1-x)
10	Out-of-Core	2	x	Coupon	FeCrAl	Kanthal AF	(none)
10	Out-of-Core	2	y	Coupon	FeCrAl	C06M	(none)
10	Out-of-Core	2	z	Coupon	FeCrAl	Kanthal AF	(none)
10	Out-of-Core	2	aa	Coupon	FeCrAl	C06M	(none)
10	Out-of-Core	2	ab	Coupon	Zr alloy	Zircaloy-4	(none)
10	Out-of-Core	2	ac	Coupon	FeCrAl	C36M	(none)
10	Out-of-Core	2	ad	Coupon	Zr alloy	Zircaloy-4	(none)
10	Out-of-Core	2	ae	Coupon	FeCrAl	C36M	(none)
10	Out-of-Core	2	af	Coupon	Coated SiC	R&H CVD SiC HR	PVD CrN(1-x)-Cr2N