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ORNL/MD/LTR-133
Level 2

**Gallium - Cladding Compatibility Testing
Plan
Phases I and II : Test Plan for
Gallium Corrosion Tests**

Revision 2

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R. N. Morris **JUL 16 1998**
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Fissile Materials Disposition Program

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Phases I and II : Test Plan for
Gallium Corrosion Tests**

Revision 2

**D. F. Wilson
R. N. Morris**

May 1998

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Gallium - Cladding Compatibility Testing Plan

Revision No.	Comments	Date issued
0	Original	2/14/97
1	Revised as a result of comments from P. Rhoads (DOE HQ), B. Steele (MPR Associates), and J. Buska (LANL)	6/2/97
2	Interim program schedule update	4/98

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ABSTRACT

This test plan is a Level-2 document as defined in the Fissile Materials Disposition Program Light-Water-Reactor Mixed-Oxide Fuel Irradiation Test Project Plan. The plan summarizes and updates the projected Phases I and II Gallium-Cladding compatibility corrosion testing and the following post-test examination. This work will characterize the reactions and changes, if any, in mechanical properties that occur between Zircaloy clad and gallium or gallium oxide in the temperature range 30–700°C.

1. INTRODUCTION

1.1 BACKGROUND

This document is an update of the previous version of the test plan and includes the updated test matrixes as well as comments on the progress to date. A great deal of work on gallium has already been performed by ORNL for the Fissile Materials Disposition Program (FMDP): *Assessment of Gallium in (U,Pu)O₂ LWR Fuels*, Terrence B. Lindemenr, July 29, 1995; *Potential Effects of Gallium on Cladding Materials*, ORNL/TM-13504, D. F. Wilson et al.; and *Interactions of Zircaloy Cladding with Gallium 1997 Status*, ORNL/TM-13305, D. F. Wilson et al. In addition, relevant material has been presented at meetings and included in monthly reports. This update is an effort to consolidate the modifications and changes made in the Phase I and II tasks.

The Fissile Materials Disposition Program (FMDP) is investigating the use of weapons-grade plutonium in mixed-oxide (MOX) fuel for light-water reactors (LWR). Commercial MOX fuel has been successfully used in overseas reactors for many years; however, weapons-derived test fuel contains small amounts of gallium. A concern exists that the gallium may migrate out of the fuel, react with the clad, and thereby promote loss-of-fuel pin integrity. Current, but limited, experimental evidence indicates that this is not likely to happen to any significant extent. However, the program still needs to determine the validity of this hypothesis.

Currently, the FMDP intends to remove the gallium during the plutonia powder conditioning prior to fuel fabrication. Investigations of powder conditioning and gallium evolution during fuel fabrication are being conducted by LANL. However, no removal technique is completely effective, so it is probable that residual gallium will be carried through fuel fabrication into the finished fuel. Therefore, it is important to understand the potential cladding interactions and the available safety margins with respect to gallium concentration for licensing and safe reactor operation. The initial gallium in the plutonium is expected to result in roughly 100 ppm gallium in the treated PuO₂, and about 1 to 10 ppm gallium in the final MOX fuel.

The proposed gallium-cladding compatibility tests in this document, presented as Phase I and Phase II, rely on surrogate testing to expedite schedule and reduce costs. Prototypic clad materials, Zircaloy-2, Zircaloy-4, and Zirlo will be evaluated. The composition ranges for Zircaloy-2 and Zircaloy-4 are presented in Table 1. Zirlo is a proprietary material. The material compositions in the table are for comparison purposes only; actual composition details may be vendor specific.

Table 1. Composition range of standard Zircalloys (wt %, except where noted)

Name	Sn	Fe	Cr	Ni	Nb	O (ppm)
Zircaloy-2 ^a	1.2–1.7	0.07–0.2	0.05–0.15	0.03–0.08		1000–1400
Zircaloy-4 ^a	1.2–1.7	0.18–0.24	0.07–0.13			1000–1400
Zirlo ^b	0.96–0.98	0.094–0.105	79–83 ppm		1.02–1.14	900–1200

^aR. W. Cahn, P. Haasen, E. J. Kramer, *Materials, Science, and Technology*, Vol. 10b, Nuclear Materials, Part 2, pp. 11, 1994.

^bG. P. Sabol, R. J. Comstock, R. A. Weiner, P. Larouere, and R. N. Stanutz, "In-Reactor Corrosion Performance of Zirlo and Zircaloy-4," pp. 724–744 in *Zirconium in the Nuclear Industry: Tenth International Symposium, ASTM STP 1245*, A. M. Garde and E. R. Bradley, eds., American Society for Testing and Materials, Philadelphia, 1994.

Even though the expected fuel concentration of gallium is low, the very limited solubility of gallium in zirconium, especially at temperatures below 700°C,¹ suggests that grain boundary penetration and liquid metal embrittlement are possible reactions. Results to date, however, indicate that these reactions are not occurring.

At present, the primary reaction is the expected formation of intermetallic compounds. Corrosion reactions are being examined in Phase I and Phase II of the planned experimental program. Phase I has characterized the types of corrosion that occur when cladding is exposed to liquid gallium. Solid-solid interactions are being evaluated in Phase II. These phases will be performed concurrently to the extent that test equipment availability allows. Corrosion reactions are being characterized as a function of time, temperature, and concentration of gallium.

Testing is being performed in the temperature range, 30–700°C, that encompasses important temperatures for the fuel-clad system: Ga₂O sublimates at ≥500°C, Ga₂O melts at ≥660°C, and gallium melts at 30°C.

1.2 OBJECTIVES AND GOALS

The objective of Phase I and Phase II testing is to characterize the corrosion reactions that occur between the clad and gallium or gallium oxide. Phase I testing will provide the microstructural information associated with interactions between the cladding and liquid gallium at various temperatures. This information will assist in interpreting the results of Phase II testing, especially as to whether any observed changes in the microstructure are the result of reactions with liquid gallium. To satisfy these objectives, the following goals must be achieved:

1. complete the design and fabrication of a series of test specimens,
2. design and construct the necessary test apparatus to properly position the specimens and ensure that they are exposed to the proper environment during testing,

3. determine the proper strain rate for the tensile tests,
4. perform post-test analyses of the test specimens as appropriate for the particular test, and
5. prepare a comprehensive report on the results of the testing.

2. PHASE I

2.1 INITIAL GALLIUM TESTING

The first tests have exposed the cladding materials of interest (Zircaloy-2, Zircaloy-4, and Zirlo) to metallic gallium in an inert, ambient-pressure atmosphere at elevated temperatures. These tests have used "partial length" welded clad tube specimens. Both static and constant extension rate tensile (CERT) tests have been performed to determine the reactions that occur, their rates, and the potential cladding failure mechanisms, especially the potential for grain boundary penetration and liquid metal embrittlement (LME). Post-test analyses of cross sections of the "partial-length" clad tubes have been performed.

In the case of CERT tests, the ductility of specimens tested in the presence of gallium has been compared with those specimens tested in the absence of gallium and the morphology of fracture surfaces have been evaluated. These tests were done within a protective chamber to provide an inert atmosphere around the tests specimens to preclude the reaction of zirconium alloys with the ambient oxygen and nitrogen during testing. Final evaluation of these tests is underway.

2.2 PHASE I TEST MATRIX

The test parameter space for Phase I experiments is shown in Tables 2 and 3. Eighteen corrosion tests of Zircaloy with gallium and 36 mechanical tests of Zircaloy with gallium will be conducted for a total of 54 Phase I tests. In addition, other tests have been conducted as necessary to determine the best design for the test specimens and to resolve problems that have arisen. Material, test type (static or stressed), time, and temperature are the major variables involved in the Phase I tests. An excess of gallium has been used in these tests to ensure that the reaction mechanisms are not limited by the availability of gallium. In general, the testing sequence has been from short-to-long times and from low-to-high temperatures.

2.3 PHASE I POST-TEST EVALUATION

After the test specimens have been exposed to the testing environment they will undergo a post-test examination to determine the effects of the exposure and/or mechanical stress. In general, the specimens will be inspected for signs of wall thinning, grain boundary penetration, and transgranular attack. The degree of gallium penetration into the clad material will be investigated, along with the thickness of any intermetallic layer. Metallographic mounts of selected specimens will be prepared; visual, scanning electron microscope (SEM), microprobe, and local hardness examinations will be conducted at the discretion of the researcher. Fracture surfaces will be examined for signs of other than ductile failure.

2.4 PHASE I MILESTONES AND DELIVERABLES

A year-end report documenting the results to date was released in November 1997 (*Interactions of Zircaloy Cladding with Gallium 1997 Status*, ORNL/TM-13505, D. F. Wilson et al.); a final report detailing the final results of all the testing will be released in September 1998. An interim report detailing progress to date will be released in May 1998.

**Table 2. Corrosion (static) tests of Zircaloy with gallium
(16 tests)**

Material	Test time (h)	Test temperature (°C) [number of specimens]				Comments/status {☐ indicates completed test}
		30	300	500		
				No cadmium	With cadmium	
Zircaloy II	200			☐ 1		Complete
	700	☐ 1	☐ 1	☐ 1		Complete
Zircaloy IV	200			☐ 1	☐ 1	All tests have been completed. Intermetallic compound formation (ICF); dimensional distortion
	700	☐ 1	☐ 1	☐ 1	☐ 1	All tests have been completed. No attack at 30 or 300°C. ICF at 500°C, but no increase in ICF amount over 200 h. Dimensional distortion
Zirlo	200			☐ 1	☐ 1	All tests have been completed. ICF; dimensional distortion
	700	☐ 1	☐ 1	☐ 1	☐ 1	All tests have been completed. No attack at 30 or 300°C. ICF at 500°C, but no increase in amount over 200 h. Dimensional distortion at 500°C

Table 3. Mechanical tests of Zircaloy with gallium ^a (36 tests)					
Material	Test type	Test temperature (°C) [number of specimens]			Comments/status {□ indicates completed test}
		30	100	300	
Zircaloy II	LME	□ 3 + Control	□ 3 + Control		Complete
	CM			□ 3 + Control	Complete
Zircaloy IV	LME	□ 3 + Control	□ 3 + Control		Complete
	CM			□ 3 + Control	Complete
Zirlo	LME	□ 3 + Control	□ 3 + Control		Complete
	CM			□ 3 + Control	Complete

^a LME constant extension rate tensile (CERT) test at temperature (0.0002 in./min.)

CM CERT test at room temperature after 30 h at temperature (0.05 in./min.)

3. PHASE II

3.1 OXIDE COMPATIBILITY TESTS

These tests are exposing cladding materials of interest (Zircaloy-2, Zircaloy-4, and Zirlo) to gallium oxide and to a MOX surrogate gallium-containing oxide compound (cerium oxide mixed with gallium oxide). These tests are evaluating the compatibility of the clad with gallium oxide in an inert, ambient-pressure atmosphere at elevated temperatures. These tests will use "partial length" welded clad tube specimens. Both static and CERT tests are being performed to determine the reactions that occur, their rates, and the potential cladding failure mechanisms, especially the potential for grain boundary penetration and liquid metal embrittlement (LME).

Test capsules are being fabricated from vendor-supplied fuel cladding tubing by welding end caps machined from Zircaloy rod stock and/or larger-diameter tubes on either end. These capsules contain gallium oxide or the MOX surrogate gallium-containing oxide compound for the compatibility testing. Capsule preparation (design, welding, etc.) is the same as was done for Phase I. The welded capsules containing gallium oxide or MOX surrogate gallium-containing oxide are being tested at temperatures (300, 500, and 700 °C) for two exposure times (6 weeks and 12 weeks). Both static and CERT tests will be performed. As in Phase I, a protective atmosphere will be used around the test specimens.

Post-test analyses of cross sections of the "partial length" clad tubes are being performed. In the case of static tests, evidence of wall thinning, grainboundary penetration, and transgranular attack, if present, will be documented. In the case of CERT tests, the ductility of specimens tested in the presence of MOX surrogate gallium-containing oxide will be compared with those tested in the absence of MOX surrogate gallium-containing oxide, the morphology of fracture surfaces will be evaluated, and evidence of grainboundary penetration and transgranular attack, if present, will be documented.

3.2 PHASE II TEST MATRIX

The planned (and completed) test parameter space for each of the five gallium levels (in the MOX surrogate cerium-gallium-oxide) to be considered in Phase II tests is given in Tables 4 and 5. This test matrix is a reduced form of the original one, with some of the 700°C tests being eliminated because of specimen distortion and guidance from DOE to confine testing to normal clad operating temperatures.

The sequence of corrosion tests of Zircaloy with Ga_2O_3 is composed of 45 tests and the sequence of corrosion-mechanical tests of Zircaloy with Ga_2O_3 is composed of 216 tests for a total of 261 tests. The variables (material, test type, etc.) indicated are identical to those for Phase I tests. The major difference is the test environment (i.e., gallium oxide and low levels of gallium oxide in a MOX surrogate mixture vs liquid gallium, as before). Also note that Phase II tests are not planned at temperatures below 300°C and that planned exposure times are significantly longer than for Phase I tests. This difference in conditions occurs because the anticipated severity of the test environment is lower and possible reaction mechanisms are likely to occur at a slower rate.

**Table 4. Corrosion (static) tests of Zircaloy with Ga₂O₃
(45 tests)**

Material	Ga ₂ O ₃ conc. (%)	Test time (weeks)	Test temperature (°C) [number of specimens]			Comments/status {□ indicates completed test}
			300	500	700	
Zircaloy II	100	6	□ 1	□ 1	□ 1	Complete
	100	12	□ 1	□ 1	□ 1	Complete
	1	6	□ 1	□ 1	□ 1	Complete
	0.2	6	□ 1	□ 1	□ 1	Complete
	0.1	6	□ 1	□ 1	□ 1	Complete
Zircaloy IV	100	6	□ 1	□ 1	□ 1	No interaction at 300°C; ZrO ₂ at 500 and 700°C; intermetallic compound formation (ICF) at 700°C
	100	12	□ 1	□ 1	□ 1	Same as for 6 weeks, except depth of interaction at 700°C
	1	6	□ 1	□ 1	□ 1	Complete
	0.2	6	□ 1	□ 1	□ 1	Complete
	0.1	6	□ 1	□ 1	□ 1	Complete
Zirlo	100	6	□ 1	□ 1	□ 1	No interaction at 300°C; ZrO ₂ at 500 and 700°C; intermetallic compound formation (ICF) at 700°C
	100	12	□ 1	□ 1	□ 1	Same as for 6 weeks, except depth of interaction at 700°C
	1	6	□ 1	□ 1	□ 1	Complete
	0.2	6	□ 1	□ 1	□ 1	Complete
	0.1	6	□ 1	□ 1	□ 1	Complete

Table 5. Corrosion-mechanical tests of Zircaloy with Ga_2O_3
(216 tests)

Material	Ga_2O_3 conc. (%)	Tensile test temp (°C)	Test time (weeks)	Test temperature (°C) [number of specimens]		Comments/status {□ indicates completed test}
				300	500	
Zircaloy II	100	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0.2	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0.1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0 [100% Cerium oxide]	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	Empty	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway

Material	Ga ₂ O ₃ conc. (%)	Tensile test temp (°C)	Test time (weeks)	Test temperature (°C) [number of specimens]		Comments/status { ☐ indicates completed test}
				300	500	
Zircaloy IV	100	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0.2	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0.1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0 [100% Cerium oxide]	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	Empty	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
Zirlo	100	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway

Material	Ga ₂ O ₃ conc. (%)	Tensile test temp (°C)	Test time (weeks)	Test temperature (°C) [number of specimens]		Comments/status {□ indicates completed test}
				300	500	
	0.2	500	6		3	Scheduled/underway
		30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0.1	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	0 [100% Cerium oxide]	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway
	Empty	30	6	3	3	Scheduled/underway
		300	6	3		Scheduled/underway
		500	6		3	Scheduled/underway

3.3 PHASE II POST-TEST EVALUATION

After the test specimens have been exposed to the testing environment, they will undergo a post-test examination to determine the effects of the exposure and/or mechanical stress. In general, the specimens will be inspected for signs of wall thinning, grain boundary penetration, and transgranular attack. The degree of gallium or oxide penetration into the clad material will be investigated, along with the thickness of any intermetallic or oxide layer. Metallographic mounts will be prepared of selected specimens; visual, scanning electron microscope (SEM), microprobe, elemental composition, and local hardness examinations will be conducted at the discretion of the researcher. Fracture surfaces will be examined for signs of other than ductile failure.

To date, only the expected intermetallic compound formation is taking place. At high temperatures and very high gallium concentrations, specimen distortion is taking place; however, at more moderate gallium concentrations (still many thousands of times greater than expected in MOX fuel), no serious effects are being seen.

3.4 PHASE II MILESTONES AND DELIVERABLES

A report documenting the results to date was released in November 1997 (*Interactions of Zircaloy Cladding with Gallium 1997 Status*, ORNL/TM-13505, D. F. Wilson et al.); a final report detailing the final results of all the testing, both Phases I and II, will be released in September 1998. In addition, an interim report, *Interactions of Zircaloy Cladding with Gallium 1998 Midyear Status*, will be released in May 1998.

4. Conduct of Operations

4.1 QUALITY ASSURANCE

This work will be conducted in accordance with the Quality Assurance (QA) Plan for the Oak Ridge National Laboratory, Y/QD-15.

4.2 NEPA

This project has been granted an NEPA categorical exclusion (CX) and has been entered into the ORNL National Environmental Policy Act (NEPA) Compliance Database.² The very small quantities of waste that will be generated will be disposed of using existing procedures.

5. SCHEDULE

5.1 REMAINING SCHEDULE

At the time of publication of this document, approximately half of the planned testing has been completed and documented in the *Interactions of Zircaloy Cladding with Gallium 1997 Status*, ORNL/TM-13505. The test schedule for the updated task (changes were implemented beginning in mid-February) is shown in Fig. 1. Previous versions of this test plan and FMDP monthly reports have detailed the past schedule and progress.

The primary risk to the schedule is caused by the long times required for the testing. A significant problem near the end of a test series can set the task back as long as the duration of the test (approximately 6 weeks or more). By batching the tests and performing more than one test at a time, this task has minimized the potential for major additional schedule disruptions.

Fig. 1. Schedule remaining for the Phase I and II work.

REFERENCES

1. Thaddeus B. Massalski, ed., *Binary Alloy Phase Diagrams*, Vol. 3, pp. 1878, 1880. ASM International, Metals Park, OH, 1990.
2. J. B. Murphy, Office of Environmental Protection, letter to D. F. Craig and D. F. Wilson, "Approved Categorical Exclusion (CX) for *Gallium-Cladding Compatibility Testing (2559X)*," May 28, 1997.