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BEHAVIOR OF ZIRCALOY CLADDING IN THE PRESENCE OF GALLIUM

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Abstract

The U.S. Department of Energy has established a dual-track approach to the disposition of plutonium arising from the dismantling of nuclear weapons. Both immobilization and reactor-based mixed-oxide (MOX) fuel technologies are being evaluated. The reactor-based MOX fuel option requires assessment of the potential impact of concentrations of gallium (on the order of 1 to 10 ppm), not present in conventional MOX fuel, on cladding material performance. An experimental program was designed to evaluate the performance of prototypic Zircaloy cladding materials against (1) liquid gallium, and (2) various concentrations of Ga_2O_3. Three types of tests were performed: (1) corrosion, (2) liquid metal embrittlement, and (3) corrosion-mechanical. These tests were to determine corrosion mechanisms, thresholds for temperature and concentration of gallium that delineate behavioral regimes, and changes in the mechanical properties of Zircaloy. Results have generally been favorable for the use of weapons-grade (WG) MOX fuel. The Zircaloy cladding does react with gallium to form intermetallic compounds at $\geq 300°C$; however, this reaction is limited by the mass of gallium and is therefore not expected to be significant with a low level (parts per million) of gallium in the MOX fuel. Furthermore, no evidence for grain boundary penetration by gallium or liquid metal embrittlement was observed.

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Introduction

Gallium initially present in WG-plutonium is largely removed during processing to produce MOX fuel. After blending the plutonium with uranium, only 1 to 10 ppm gallium is expected in the sintered MOX fuel. Gallium present as gallium oxide (Ga_2O_3) could be evolved as the suboxide (Ga_2O). Migration of the evolved Ga_2O and diffusion of gallium in the MOX matrix along thermal gradients could lead to locally higher concentrations of Ga_2O_3. Thus, while an extremely low concentration of gallium in MOX fuel almost ensures a lack of significant interaction of gallium with Zircaloy fuel cladding, there remains a small probability that corrosion effects will not be negligible.

General corrosion in the form of surface alloying resulting from formation of intermetallic compounds between Zircaloy and gallium should be mass limited and, therefore, superficial because of the expected low ratio of gallium to the surface area or volume of the Zircaloy cladding. Although the expected concentration of gallium is low and there is very limited solubility of gallium in zirconium, especially at temperatures below 700°C,[1] grain boundary penetration and liquid metal embrittlement (LME) are forms of localized corrosion that were also considered.

One fuel system damage mechanism, pellet clad interaction, has led to some failure of the Zircaloy cladding in light-water reactors (LWRs). This has been attributed to stresses in the cladding and one or more aggressive fission products. Stress corrosion cracking by iodine[2, 3] and LME by cadmium[4, 5] have been reported, and it is known that Zircaloy can be embrittled by some low-melting metals, (e.g., mercury).[6] LME is a form of environmentally induced embrittlement that can induce cracking or loss of ductility. LME requires wetting and a tensile stress, but it does not require corrosion penetration. Experimentally, it has been demonstrated that gallium can cause embrittlement of some alloys (e.g., aluminum) at low temperatures,[7, 8] but experiments relative to LME of zirconium by gallium have been limited and inconclusive.[9]

The overall objective of this task is to demonstrate the effects of small concentrations of gallium in MOX fuel on the performance of the fuel system in an LWR. Although possible mechanisms for gallium interaction with Zircaloy have been identified,[10] no significant data exist that demonstrate whether such reactions actually occur under LWR conditions and whether these reactions have any significant effects on cladding performance. A graded, experimental approach was designed to determine whether low levels of gallium would result in damage to the fuel clad. First, laboratory tests were conducted on three prototypic Zircaloy cladding materials in liquid gallium. Three types of tests were used: (1) corrosion, (2) LME, and (3) corrosion-mechanical. Corrosion tests consisted of time–temperature exposures of Zircaloy to liquid gallium. LME tests consisted of slow strain rate, constant extension rate tensile (CERT) tests in gallium metal at low temperature (30 and 100°C). Corrosion-mechanical tests consisted of first exposing the Zircaloy to gallium metal and then conducting a tensile test to evaluate corrosion product effects. Although these tests conditions (much higher relative amount of gallium compared with that in a fuel rodlet) are not representative of WG-MOX, they provide limiting boundary conditions for mechanistic studies.

Secondly, two of the previously mentioned types of tests, corrosion and corrosion-mechanical, were conducted with the three cladding materials in contact with Ga_2O_3. In each type of test, four concentrations of Ga_2O_3 in Ce_2O_3 (surrogate for plutonium dioxide) were evaluated: 100, 1, 0.2, and 0.1 weight (wt) %. Although these levels of Ga_2O_3 are all considerably higher than those possible in a sintered MOX pellet,[11] they can be used to determine the types of reactions that could occur, and, like the liquid gallium tests, they represent a conservative evaluation of Ga_2O_3 effects in this screening test phase.

Experimental

Prototypical, vendor-supplied LWR cladding materials evaluated included Zircaloy-2, Zircaloy-4, and Zirlo. Zircaloy tubing was machined into two different lengths, one for corrosion tests and another for LME or corrosion-mechanical tests, as shown in Fig. 1. End caps with and without threaded ends were machined from Zircaloy bar stock for tensile and corrosion tests, respectively. First, one end cap was welded to the specimen tube, a predetermined quantity of reactant was then added, and the other end cap was welded in place. Because of the reactive nature of the zirconium alloys with oxygen and nitrogen, all welding was performed in either high vacuum using the electron beam welding process or in a high-purity, helium-purged welding chamber using the laser beam welding process. The completed test specimens for corrosion tests were encapsulated in an evacuated quartz capsule for atmospheric protection during high-temperature exposure (Fig. 1). For mechanical testing above 100°C, a vacuum chamber with induction heating was used to preclude reaction of the zirconium alloys with ambient oxygen and nitrogen during testing. For the LME tests, the specimen was heated using copper coils containing glycol from a recirculating constant temperature bath.

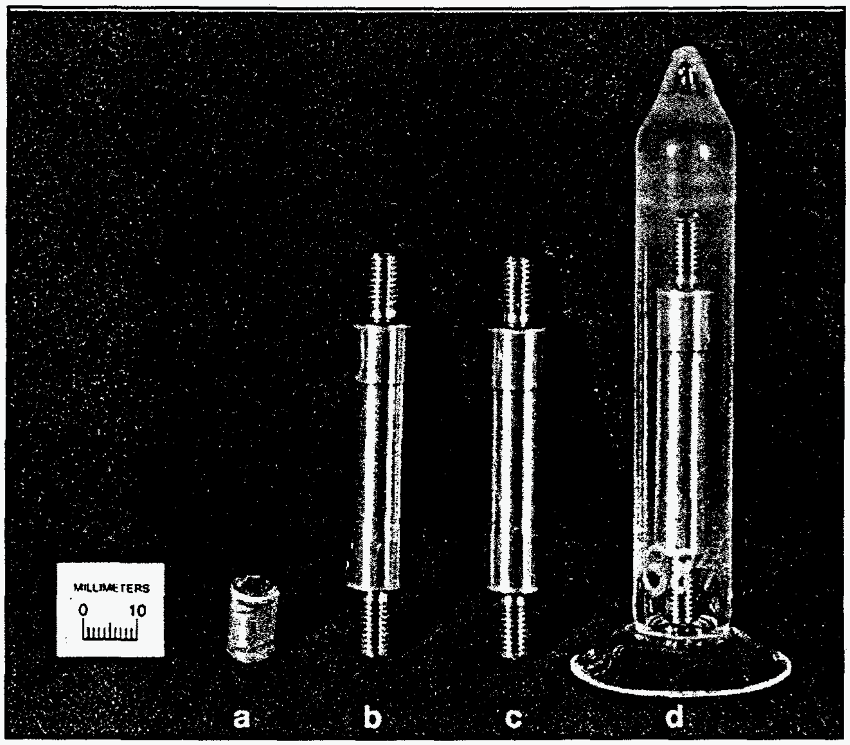


Fig. 1. Test specimens. a, corrosion; b, LME; c, corrosion-mechanical; d, encapsulated in quartz.

In addition to preliminary tests that were performed at 400 and 600°C, corrosion tests in liquid gallium were conducted at three temperatures (30, 100, and 500°C) for two exposure times (200 and 700 h). Ga_2O_3 or surrogate gallium-containing oxide tests were also conducted at three temperatures (300, 500, and 700°C) for two exposure times (6 and 12 weeks). LME tests were conducted in liquid gallium at 30 and 100°C. Corrosion-mechanical tests in liquid gallium were conducted by first exposing the Zircaloy for 30 h at 300°C and then conducting tensile tests at room-temperature. With Ga_2O_3, tensile tests were conducted at room temperature after exposure for 6 weeks at 300 and 500°C. The temperature range brackets the normal, operating clad temperature of 374°C.

These tests were intended to characterize the types of gallium–cladding interaction that occur and determine how these interactions might affect cladding properties. Thus, the amount and distribution of gallium was significantly different than would occur in a fuel pin as indicated in Fig. 2. The MOX fuel consists of a high density, sintered pellet with a very small quantity (ppm level) of gallium. In contrast, these tests contain either 100% Ga (liquid or oxide) or low density powder mixtures of Ga_2O_3 with Ce_2O_3.

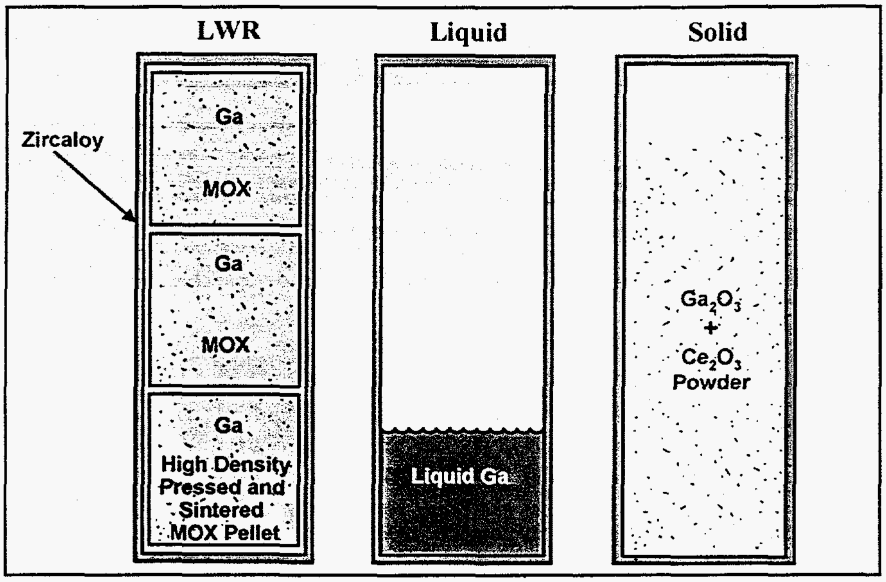


Fig. 2. Out-of-reactor tests were not prototypic of LWR fuel system relative to density and gallium concentration.

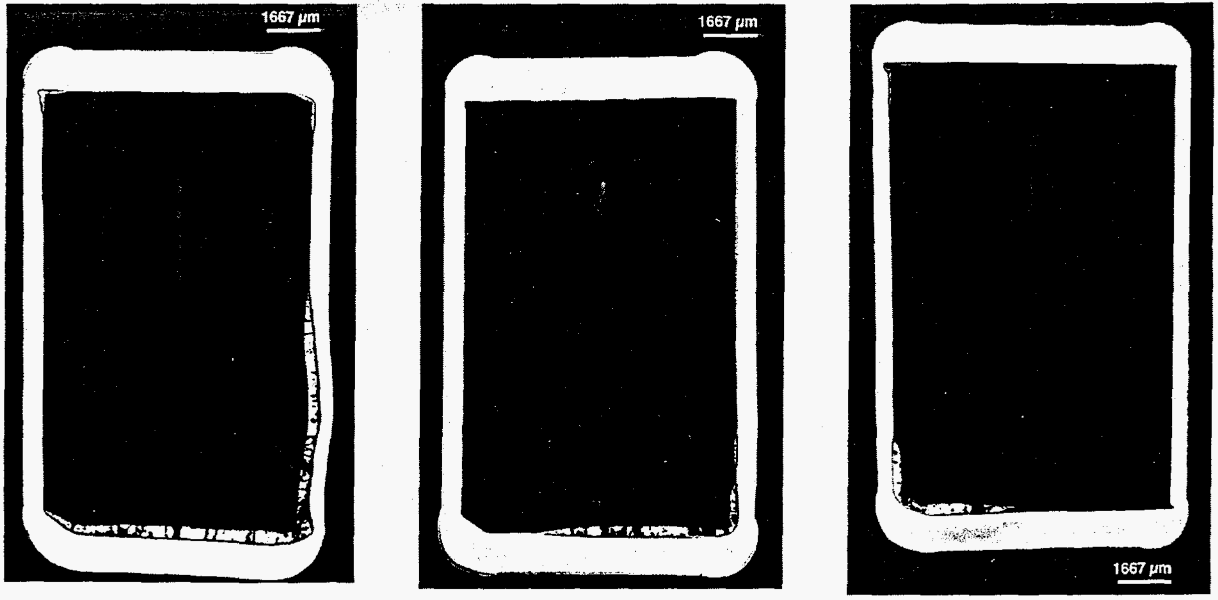
Posttest analyses of cross sections of the clad tubes included metallography, fractography, and chemical microprobe. In the case of the corrosion tests, evidence of wall thinning, grain boundary penetration, transgranular attack, and intermetallic compound formation (ICF), when present, were documented. For the mechanical tests (LME or corrosion-mechanical), the tensile strength and ductility of specimens tested in the presence of gallium or after exposure to gallium were compared with those tested in the absence of gallium.

Results

Liquid Gallium Corrosion Tests

In preliminary corrosion tests of zirconium by liquid gallium at 400°C and Zircaloy-2 (nonvendor-supplied) at 600°C, ICF was found as would be predicted from the gallium-zirconium phase diagram. Electron beam microprobe analysis identified several intermetallic compounds which were hard and brittle.

After exposure to liquid gallium for 700 h at 30 and 100°C, none of the Zircaloy materials showed evidence of significant interaction. At 500°C, all of the gallium reacted with Zircaloy to form intermetallic compounds (ICs) of the type Zr_xGa_y after 200 or 700 h. Dimensional distortion of some Zircaloy capsules was observed as a result of exposure at 500°C. Subsequent investigation revealed that the amount of distortion was a function of the amount of gallium initially in the capsule even though there was considerable empty space remaining within the capsule at the end of the test (Fig. 3). One of the Zircaloy materials showed little or no distortion even at the highest amounts of gallium, despite the fact that a Zr_xGa_y type of IC formed. Comparisons of the corrosion products at high magnifications showed some differences in the appearance of the ICs. Where no distortion occurred, the corrosion product was more porous than where distortion did occur. Further testing at temperatures below 500°C showed that, in the susceptible materials, dimensional distortion also occurred at 400 and 350°C but was not found after 200 h at 300°C. After 200 h at 300°C, there was a large amount of unreacted gallium in the capsule at the end of the test.



a b c

Fig. 3. Corrosion testing with smaller amounts of gallium (Ga) at 500°C for 200 h. a = 0.2 g Ga, shows a small amount of dimensional distortion; b = 0.09 g Ga, shows minor dimensional distortion; c = 0.05 g Ga, shows no dimensional distortion.

As indicated in Fig. 3, dimensional distortion at 500°C was eliminated when smaller amounts of gallium were used in the capsule. In subsequent tests at 500°C with even smaller quantities of gallium (0.025 to 0.00038 g), ICF was localized to specific regions where gallium chemically wet the capsule wall but the depth of interaction was quite shallow.[12, 13]

Liquid Metal Embrittlement Tests

CERT tests (3.33×10^{-6}/s) were conducted in gallium at 30 and 100°C, and the results (average of three specimens per condition) for Zircaloy C are shown in Figs. 4 and 5. No differences in the tensile properties were found between the tests in gallium compared with those at the same temperature without gallium for any of the Zircaloy materials tested. Although there was a small decrease in strength from 30 to 100°C, this same change occurred without gallium as well. Furthermore, the specimens all failed in a ductile manner, as shown in Fig. 6.

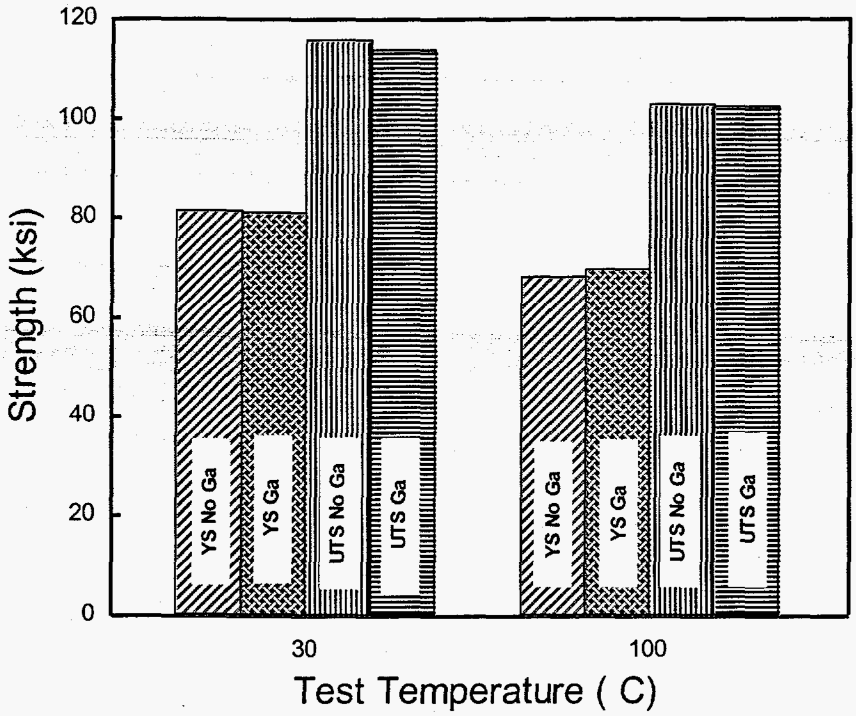


Fig. 4. LME test showed no change in strength for Zircaloy C at 30 and 100°C. YS, yield strength; UTS, ultimate tensile strength.

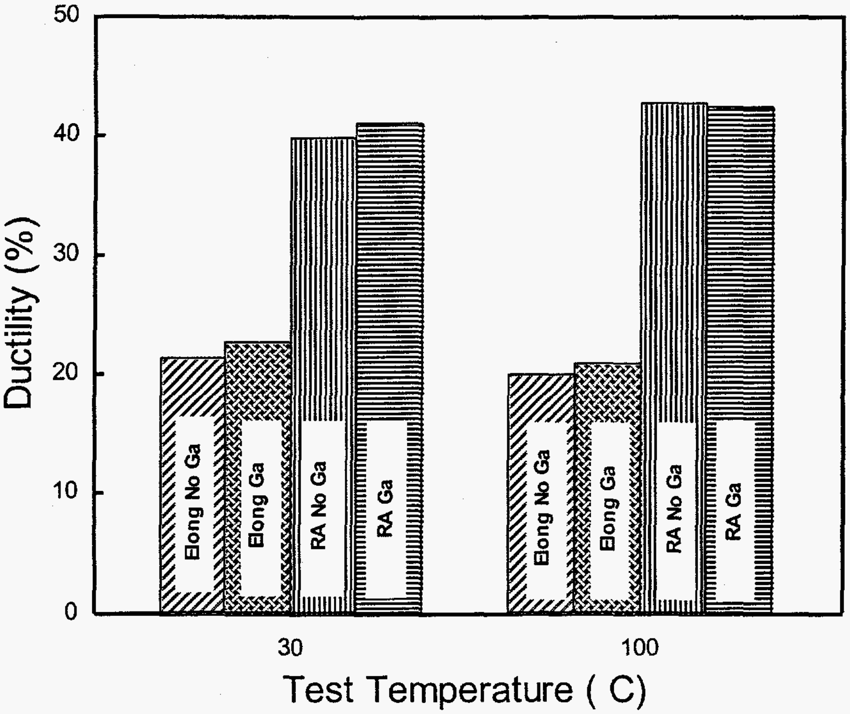


Fig. 5. LME tests showed no significant difference in ductility for Zircaloy C at 30 and 100°C. Elong, elongation; RA, reduction in cross sectional area.

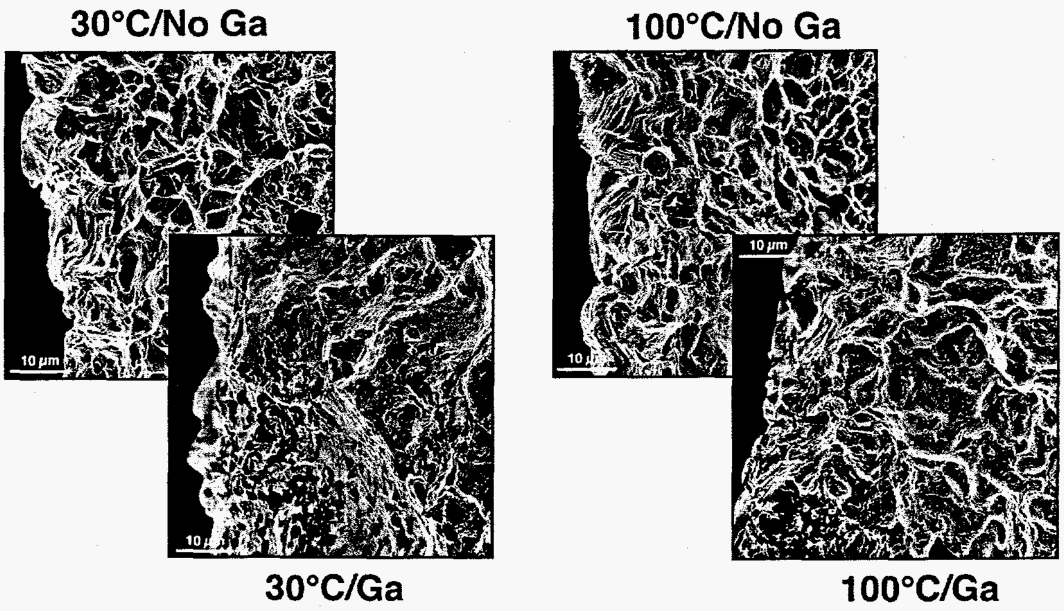


Fig. 6. Ductile failure mode at 30 and 100°C with and without gallium.

Liquid Gallium Corrosion-Mechanical Tests

The purpose of these tests was to obtain some measure of the effect of ICF on the mechanical properties of Zircaloy. The Zr_xGa_y IC is quite hard and brittle; therefore, significant (and unrealistically large) quantities of ICF would be expected to markedly affect the mechanical properties of the Zircaloy. Based on prior data from the corrosion tests, exposure of the Zircaloy to gallium for 30 h at 300°C was ultimately selected as the condition for the corrosion portion of the corrosion-mechanical tests. Under these conditions, most of the gallium did not react with the Zircaloy; however, a thin, intermittent area of ICF was present along the gage length of the Zircaloy capsule specimen. CERT tests (8.33×10^{-4}/s) were conducted at room temperature. The results (average of three specimens per material, per condition) indicate very little, if any, effect of the formation of small amounts of ICF on the mechanical properties of Zircaloy. In addition, examination of the fracture surfaces did not indicate any significant difference in the mode of failure.

Gallium Oxide Corrosion Tests

Corrosion tests in nonprototypic, powder mixtures containing Ga_2O_3 were conducted at 300, 500, and 700°C for 6 and 12 weeks. Ce_2O_3 powder was mechanically blended with Ga_2O_3 powder to produce mixtures that contained 100, 1, 0.2, 0.1, and 0 wt % Ga_2O_3 to assess the effect of the concentration of gallium present during the exposures. There were significant differences among results at the three temperatures. At 300°C, no significant reaction was noted except for very slight surface roughening, even after the 12-week exposures. At 500°C, additional tests of Zircaloy were conducted with ZrO_2 and CaO as well, and an oxide layer was observed in all of the tests.[12,13] In the Ce_2O_3-Ga_2O_3 tests, the thickness of the oxide layer was independent of Ga_2O_3 concentration and did not appreciably increase with time between 6 and 12 weeks. A visually distinguishable zone was noted below the oxide layer. Although this zone was larger for the tests with 100% Ga_2O_3, there was no appreciable difference among 1, 0.2, and 0.1% Ga_2O_3 exposures. At 700°C, there was formation of an oxide layer on the inner surface of the

Zircaloy and an identifiable gallium-rich zone below the oxide layer. The thickness of both the oxide and gallium-rich zone increased with time, but the gallium-rich zone was visible only with 100% Ga_2O_3. Another feature not seen at 500°C is cracking of the Zircaloy. Generally, testing at 700°C resulted in a somewhat uniform distortion of the Zircaloy tubing, and the cracks may be associated with an oxygen-enriched zone.

Gallium Oxide Corrosion-Mechanical Tests

The results of CERT tests (8.33×10^{-4}/s), conducted at room temperature, are shown for one of the alloys (Zircaloy C) in Figs. 7 and 8. There was either a slight change or no change in the room-temperature tensile properties (three specimens per condition) of any of the Zircaloy materials after exposure at 300°C, as would have been predicted based on the corrosion test results reported previously. Similarly, after exposure at 500°C, there was little change in the room-temperature properties as a function of Ga_2O_2 concentration, but both room temperature yield and ultimate tensile strength (Fig. 7) were lower than after exposure at 300°C for two of the three Zircaloys for all Ga_2O_3 concentrations, with a corresponding increase in ductility as measured by elongation and reduction in area (Fig. 8). Control tests indicated that these changes are a result of heat treatment at 500°C instead of the test environment. Before heat treatment at 500°C, two of the alloys (Zircaloys B and C) had room-temperature tensile properties similar to those shown for heat treating/exposure to oxide powder at 300°C. Thus, the heat treatment of these alloys at 500°C reduced their strength and increased their ductility. The properties of the third alloy, Zircaloy A, were little changed by the 500°C heat treatment.

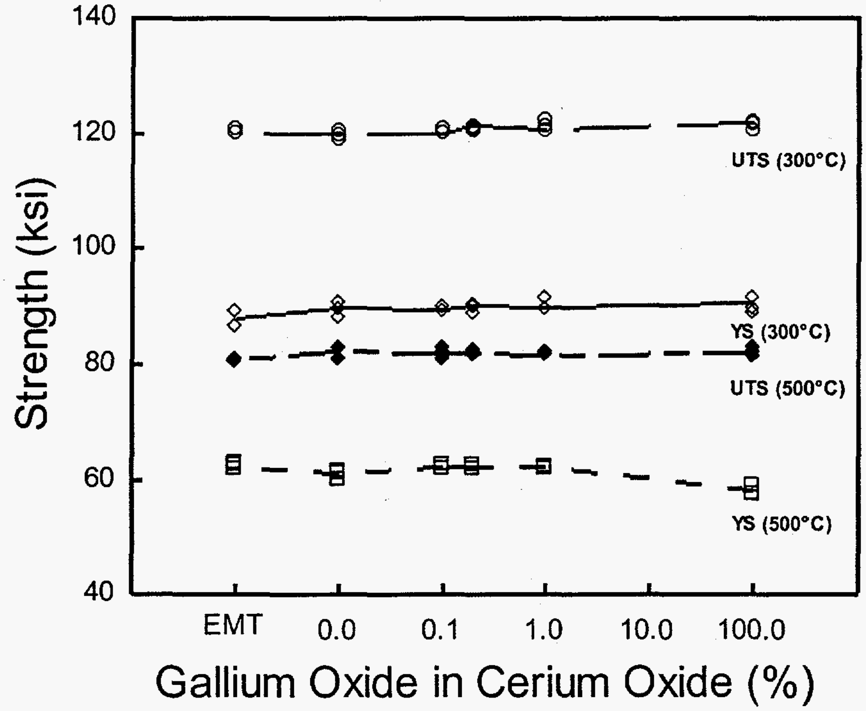


Fig. 7. No significant change in room-temperature strength for Zircaloy C after exposure to Ga_2O_3 in cerium oxide (6 weeks at 300 and 500°C). YS, yield strength; UTS, ultimate tensile strength; EMT, empty.

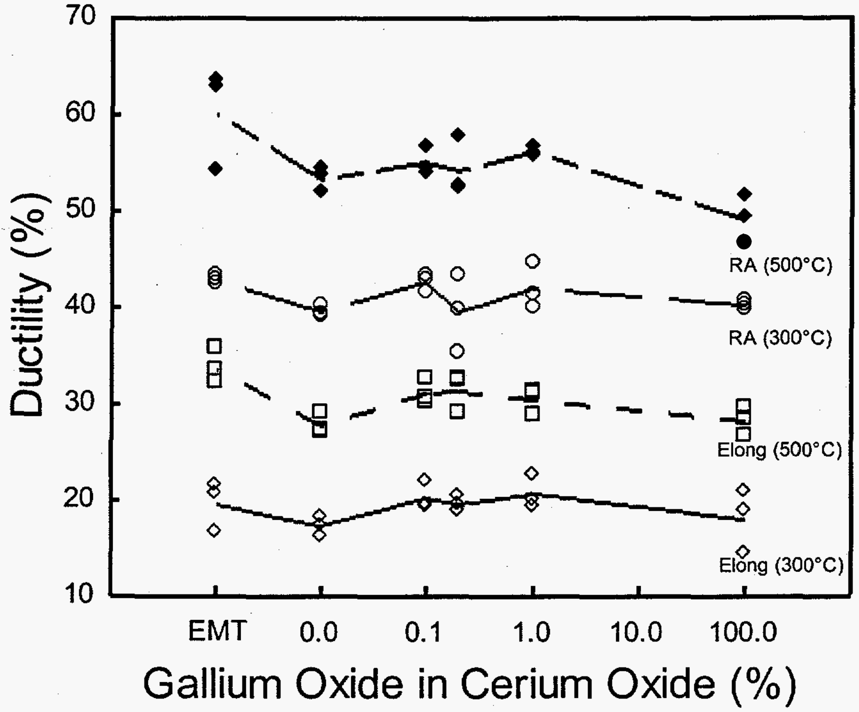


Fig. 8 . Slight change in room-temperature ductility for Zircaloy C after exposure to Ga_2O_3 in cerium oxide (6 weeks at 300 and 500°C). Elong, elongation; RA, reduction in cross-sectional area; EMT, empty.

Discussion

Liquid gallium is highly reactive with most metals since it readily alloys with elemental components that are in many structural materials. For example, gallium forms intermetallic compounds with iron, nickel, chromium, cobalt, vanadium, and zirconium. Even though these elements have limited solubility in gallium at temperatures as high as ~500°C, they would not be suitable for use in structural materials to contain gallium above 300°C because of their chemical conversion to ICs of the form M_xGa_y, where M_x refers to a metallic element. However, in the present application, in which the total amount of gallium in a 3.66-m (12-ft) fuel pin is expected to be ~0.02 g, formation of ICs would be very limited. If in the unlikely event that all of the gallium present in a fuel pin were to reach the cladding interface in one location, only a very small amount of the cladding wall would be converted to ICs and the effect on tensile properties will be slight to negligible. These studies have also shown no embrittlement of Zircaloy caused by either classic LME effects from liquid gallium or reactions that result in the formation of small amounts of ICF or an oxide layer on the Zircaloy.

LME is a phenomenon similar to stress corrosion cracking that can occur with certain liquid metal–solid metal combinations. However, the kinetics and mechanisms of LME are not clearly understood. One explanation is that chemisorption of the liquid reduces bond cohesion at the surface,[14, 15] or that chemisorption creates dislocations at the tip of a crack that subsequently interact with the dislocation structure in the plastic zone leading to further microcracking.[16, 17] Wetting by the liquid metal and the presence of a tensile stress are necessary for LME to occur, but if the component elements form stable, high-melting-point compounds, severe LME is unlikely.[18, 19] Because zirconium readily forms a series of ICs with gallium at temperatures to 800°C, its resistance to LME is not surprising.

On the other hand, ICF results in conversion of zirconium in Zircaloy to a brittle intermetallic phase, which could affect the mechanical properties of the cladding. However, after reaction at 300°C to form a thin layer of IC on the inner diameter surface of the Zircaloy (but more than expected in a fuel pin), there was no effect on the tensile properties. When a similar experiment was conducted at 350°C and the thickness of the IC increased, a modest loss in ductility was found. This finding further supports a conclusion that gallium effects are mass limited.

The distortion that results from ICF appears to be related to stresses that develop in the wall of some types of Zircaloy tubing during interalloying. In preliminary tests at 400 to 600°C with either pure zirconium or nonvendor supplied Zircaloy II, no distortion was noted with quantities of liquid gallium that later caused distortion in two of the three vendor-supplied materials. Differences associated with the type of Zircaloy tested were the appearance of much more porosity in the outer IC that formed and less cracking of the inner IC where distortion was not observed. In the materials where distortion occurred, the IC was more dense and exhibited numerous cracks usually in a direction perpendicular to the wall. As the quantity of gallium available to react with the Zircaloy was reduced, distortion was eliminated. For small quantities of gallium at ≥ 350°C, the liquid gallium is quickly consumed to locally form IC, thus ending the reaction. However, when additional (excess) gallium is available, further reaction can occur as the zirconium and gallium continue to react. It is very likely that liquid gallium either diffuses through the first IC that forms or reaches the metal-IC interface via cracks in the IC. It is during this process that stresses likely develop and lead to distortion. It is well known from oxidation studies that certain volume ratios of corrosion product (oxide) to metal can lead to tensile stresses in the metal.[20]

Most probably, though not certainly, gallium will be present in MOX fuel as an oxide rather than in metallic form.[10] In corrosion tests involving oxides (Ga_2O_3, Ce_2O_3, CaO, or ZrO_2) in contact with Zircaloy, formation of zirconium oxide at the metal-oxide interface was found at 500°C. With Ga_2O_3, gallium was present below the oxide at 500°C. At 700°C, Zr_xGa_y was identified below the oxide. Because zirconium forms a very stable oxide (Fig. 9), oxide formation on the fuel cladding inner diameter surface is likely, although the rate of formation at temperatures below 500°C is unknown (e.g., at 300°C there was very slight indication of oxide formation after 12 weeks).

The room-temperature, 300, and 500°C tensile test results after exposure to oxide (Ga_2O_3 in Ce_2O_3) for 6 weeks at 300 or 500°C (temperatures that bracket the expected LWR clad normal operating temperature of ~400°C) do not appear to indicate any appreciable effect of concentration of Ga_2O_3 on strength or ductility. Two of the Zircaloy materials showed significant changes in room-temperature properties from heat treatment at 500°C. However, there were no further effects attributable to exposure to the various concentrations of Ga_2O_3 for 6 weeks.

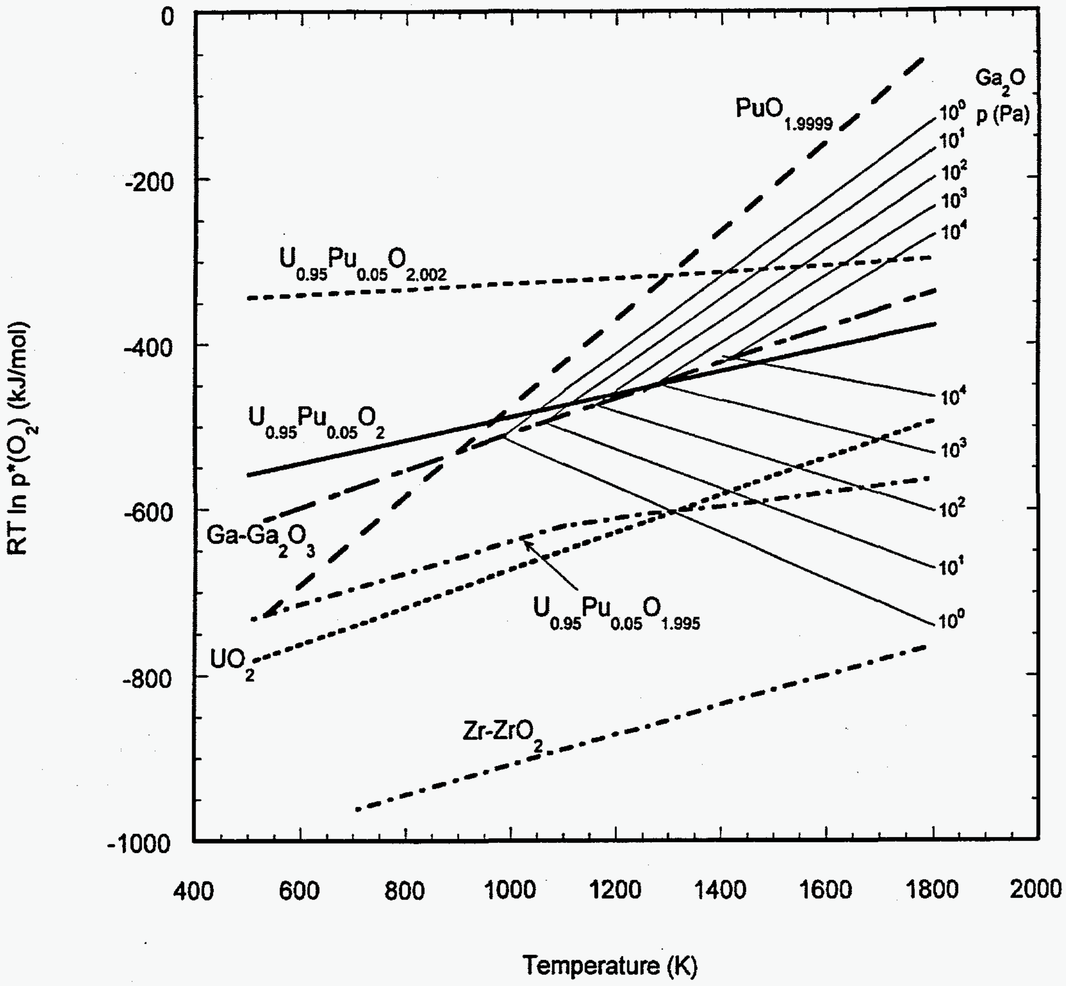


Fig. 9. Phase stability diagram for oxides of interest.[10]

Conclusions

Corrosion testing revealed that liquid gallium reacts with Zircaloy to form an IC of the form Zr$_x$Ga$_y$. The extent of reaction is a function of temperature, but more importantly, is strongly dependent on the amount of gallium involved. Although distortion of some Zircaloys can be a by-product of ICF at >300 °C, distortion in susceptible materials at 500 °C did not occur at ratios of weight of gallium to surface area of Zircaloy that were 10^4 to 10^5 higher than those expected with WG-MOX fuel in an LWR fuel pin. Mechanical property testing after corrosion exposure to form a thin IC layer on the gage section of Zircaloy specimens further confirmed that there should be little effect of small quantities of gallium in MOX fuel on the Zircaloy cladding.

No localized corrosion effects were found. In the corrosion tests (up to 500 °C), there was no evidence of grain boundary attack in addition to ICF. In the LME tests at 30 and 100 °C, there was no change in the tensile properties when Zircaloy was tested in liquid gallium and the fracture remained ductile.

Results of testing in Ga_2O_3 or Ce_2O_3-Ga_2O_3 mixtures did not indicate any significant effects at 300°C. At 500°C, an oxide layer formed on the Zircaloy and room-temperature tensile tests for two of the materials showed a loss in strength with a corresponding increase in ductility. The oxide layer also formed during exposure of Zircaloy to several other oxide powders, making it uncertain whether any of the observed mechanical effects are related to the presence of gallium.

At 700°C, which is considerably above LWR operating temperatures, there was evidence of reduction of Ga_2O_3 by Zircaloy and formation of a gallium-rich corrosion product below the ubiquitous oxide layer. However, this gallium-rich zone was not confirmed in tests with <100% Ga_2O_3.

Based on the results obtained, it does not appear that 1 to 10 ppm gallium in MOX fuel will have any measurable effect on the properties of Zircaloy cladding.