Lawrence Berkeley National Laboratory

Recent Work

Title

OXYGEN EMBRITTLEMENT OF ZIRCALLOY-2 ON LONG-TERM EXPOSURE TO ALKALINE EARTH AND RARE EARTH OXIDES

Permalink

<https://escholarship.org/uc/item/07n8t00g>

Author

Kohli, R.

Publication Date

1981-07-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to the Journal of Materials Science

OXYGEN EMBRITTLEMENT OF ZIRCALOY-2 ON LONG-TERM
EXPOSURE TO ALKALINE EARTH AND RARE EARTH OXIDES

Rajiv Kohli

July 1981

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*

LBL-12993
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-12993

OXYGEN EMBRITTLEMENT OF ZIRCALOY-2
ON LONG-TERM EXPOSURE TO ALKALINE EARTH
AND RARE EARTH OXIDES

by Rajiv Kohli

Materials and Molecular Research
Division of the Lawrence Berkeley
Laboratory and the
Department of Nuclear Engineering
University of California, Berkeley
Berkeley, California 94720

This work was supported by the Director, Office of Energy Research
Office of Basic Energy Sciences, Materials Sciences Division of the
U.S. Department of Energy under contract # W-7405-ENG-48.

ABSTRACT

The effect of long term exposure (to 10.8 Ms) of Zircaloy-2 to BaO, SrO, CeO₂, La₂O₃, Gd₂O₃, and Y₂O₃ at 623 and 973 K has been studied. The results of room temperature tensile tests show that the specimens were severely embrittled irrespective of the oxide environment, although annealing times longer than 3.6-5.4 Ms were needed for embrittlement at 623 K. Embrittlement is due to the presence of a nonstoichiometric double oxide on the surface, which facilitates the transfer of oxygen from the oxides to the metal.

One of the enduring problems in the Pellet-Clad-Interaction (PCI) failure of zircaloy-clad LWR fuel rods is the nature of the chemical environment involved in such failures. As part of an extensive investigation to address just this problem, we have tested a variety of fission product environments for activity in the embrittlement of Zircaloy-2 [1,2]. Zircaloy-2 has by weight 1.5% Sn; 0.15% Fe; 0.08% Cr; 0.05% Ni; rest Zr. Over 26% of the fission products generated during irradiation of the fuel rods consist of the alkaline earths, Ba and Sr, the rare earths, Nd, Ce, and La, and Y [3]. They will exist primarily as the oxides in the fuel rods [3]. Although these oxides are relatively nonvolatile (vapor pressures of the binary oxides are of the order of 10^{-6} MPa at 2000 K[3]) and are not expected to migrate to the cladding, their presence in the UO_2 fuel could dramatically alter the oxygen potential and, in turn, the oxidation response of the inside surface of the zircaloy cladding. The presence of Gd_2O_3 in UO_2 fuel rods, for example, has been found to enhance the oxidation rate of zircaloy cladding [4]. Since the fuel rods are operated for long times, these effects could become quite significant over the operating lifetimes. Finally, it was of interest to know if other thermodynamically more stable rare earth sesquioxides would react with zircaloy, since we have previously shown that Nd_2O_3 embrittles Zircaloy-2 [2]. The purpose of this paper is to present some results of slow strain rate tensile tests on Zircaloy-2 specimens after long-term exposure to SrO , BaO , CeO_2 , La_2O_3 , Gd_2O_3 , and Y_2O_3 .

Uniaxial tensile tests at room temperature were performed on

Zircaloy-2 flat tensile specimens (1.016 mm thickness) which had been annealed in the individual oxide powders (purity > 99.5%) at 623 and 973 K for times from 0.18 to 10.8 Ms (50 - 3000 hours). The degree of embrittlement was determined by comparing the results of annealing in the oxides with those on identical specimens annealed in high-purity argon, in terms of the fracture morphology and of variation of the tensile properties with the annealing parameters.

Even at the low annealing temperature of 623 K the specimens were severely embrittled, irrespective of the oxide environment, although annealing times longer than 3.6 - 5.4 Ms (1000 - 1500 hours) were needed for embrittlement to occur (Fig. 1). The specimens broke with a reduction of area of less than 5%, as compared with over 75% for the samples annealed in the argon environment. Figures 2 and 3 show typical fracture surface morphologies of specimens from argon and the oxide environment, respectively. The fracture in argon is completely ductile. This is mostly true of the specimens annealed in the oxides for times to 3.6 Ms (1000 hours), although some intergranular cracks can also be observed, Fig. 3a. By contrast, the fractures are completely intergranular on longer exposure, Fig. 3b.

Since these oxides were severely embrittling to the zircaloy specimens even at 623 K, the degree of embrittlement was expected to be greater at 973 K. Hence, all annealing at 973 K was limited to a maximum of 1.8 Ms (500 hours). Not surprisingly, the specimens were completely embrittled after only 0.18 Ms (50 hours) exposure. In fact, the specimens annealed in La_2O_3 , Gd_2O_3 , Y_2O_3 , and CeO_2 were so brittle that they broke during clamping in the tensile testing machine and no

tensile tests could be performed. Fig. 4 is an example of the fracture surface of such a specimen broken by hand. It shows a bald surface, characteristic of brittle failure due to through-section embrittlement. In the case of SrO and BaO, the specimens still retain some ductility even after 1.8 Ms annealing (Fig. 5), although the fracture morphology (Fig. 6) is essentially indistinguishable from the morphology on longer exposure at 623 K (Fig. 3d).

These results can be explained as follows. Thermodynamically the sesquioxides are more stable than ZrO_2 [3], and Zircaloy-2 should not react with these oxides. By x-ray diffraction, we identified ZrO_2 and $M_2Zr_2O_7$ ($M = La, Gd, Y$) as the products formed on the metal surface. In the ZrO_2 - M_2O_3 systems [5] there exists a range of homogeneity. This means that during the annealing process ZrO_2 and a nonstoichiometric double oxide form on the surface, which then serves as the means of transferring oxygen from the sesquioxide to the metal with subsequent dissolution into the metal. Also, cracks in the surface oxide provide easy paths for transport of oxygen (Fig. 7). At 623 K, the rate of diffusion of oxygen is relatively slow and longer annealing times are needed to dissolve enough oxygen (> 5 wt % [6]) in the metal to embrittle it. At 973 K, the rate of diffusion is very rapid and enough oxygen will have dissolved in the specimens after only 0.18 Ms (50 hours) to cause complete embrittlement. CeO_2 , by contrast, is thermodynamically unstable with respect to Zr [3]. Thus, oxygen will be much more easily available to react with the zircaloy specimens, forming ZrO_2 and the double oxides $Ce_2Zr_2O_7$ and $Ce_2Zr_3O_{10}$. In the case of SrO and BaO, the zirconates, $SrZrO_3$ and $BaZrO_3$, were the only

compounds formed on the metal surface. The surface layer was highly cracked, which, as noted earlier, provides easy transport paths for diffusion of oxygen. The fact that the specimens retain some ductility after exposure to SrO and BaO even at 973 K suggests that oxygen may be less readily available. Thermodynamically SrO and BaO are more stable than ZrO_2 [3] and the surface layers consist of the zirconates only. During annealing the MO - MZrO_3 (M = Sr, Ba) system will be relatively stable (there are no known nonstoichiometric compounds in the M-Zr-O system) and transfer of oxygen from the oxide to the metal will be more difficult.

As mentioned earlier, these oxides could affect the oxidation response of the zircaloy cladding, a not insignificant consideration over the operating lifetime of the fuel rods. And, as the present results have shown, even at 623 K these oxides embrittle zircaloy. Although the cladding is not exposed directly to these fission product oxides during reactor operation, more research is clearly needed to establish the effect of these oxides on zircaloy, especially in UO_2 fuel doped with these oxides. Such research is in progress.

Acknowledgments

This research was performed in conjunction with the Austrian Research Center, Seibersdorf. The author is grateful to Dr. Friedrich Holub and Professor Peter Ettmayer for useful discussions. He would like to thank Paul Reithmayr and Peter Scholze for help with the experimental work, and Carolyn Hayes and Gloria Pelatowski for assistance with manuscript preparation. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract # W-7405-ENG-48.

References

1. R. Kohli and F. Holub, Nucl. Technol. 47 (1980) 70.
2. R. Kohli and F. Holub, J. Nucl. Mater 98 (1981) 116.
3. R. Kohli, Ein thermodynamischer Beitrag zum Verständnis des Vielstoffsystems Urandioxid - Spaltprodukte - Zircaloy, Austrian Research Center Report SGAE - 3014, December 1978.
4. R. Manzel, W. Dörr, R. Würtz, Reaktortagung 1980, p. 574.
5. O. Kubaschewski (ed), Zirconium: Physico-Chemical Properties of its Compounds and Alloys, Atomic Energy Rev., Special Issue No. 6, IAEA, Vienna, 1976.
6. W. Kaden and W. Debray, Zirconium in the Nuclear Industry, ASTM STP 458, American Society for Testing and Materials, 1969, p. 179.

XBL 816-5985

Figure 1. Variation of Tensile Properties as a Function of Annealing Time for Zircaloy-2 Specimens Exposed to Argon and the Oxides at 623 K.

XBD816-5875

Figure 2. Fracture Surface of a Specimen Annealed at 973 K for 1.8 Ms in Argon.

XBB816-5877

Figure 3.(a) Scanning Electron Micrograph of the
Fracture Surface of Specimens Annealed
at 623 K in SrO, 3.6 Ms

XBB816-5878

Figure 3.(b) Scanning Electron Micrograph of the Fracture Surface of Specimens Annealed at 623 K in SrO, 10.8 Ms.

XBB816-5434A

Figure 4. Fracture Surface of a Hand-Broken Zircaloy-2 Specimen
Annealed in La_2O_3 at 973 K for 1.8 Ms.

XBL816-5986

Figure 5. Variation of the Tensile Properties as a Function of Annealing Time for Zircaloy-2 Specimens Exposed to Argon and the Oxides at 973 K.

XBB816-5876

Figure 6. Fracture Surface of a Specimen Annealed in SrO at 973 K for 1.8 Ms.

XBB816-5435

Figure 7. Optical Micrograph of a Specimen Annealed in La_2O_3 at 973 K for 1.8 Ms Showing Cracks in the Surface Oxide (Magnification: 450 times).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720