Microbeam X-ray Fluorescence Study of Alloying Elements in the Matrix of Zr Alloys

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Introduction

The concentration and distribution of the transition elements Fe, Cr and Ni present in the α-Zr matrix of Zr alloys used for nuclear fuel cladding have been linked to several in-reactor degradation processes. In particular, enhanced levels of Fe in the matrix have been shown to change the intrinsic diffusion coefficient of Zircaloy and to influence the nucleation of <c>-component loops, which can accelerate irradiation growth.[1] Understanding these links mechanistically requires the measurement of the very low alloying element concentrations in the matrix. However, the concentrations of alloying elements are below the resolution limits of traditional techniques, such as energy dispersive x-ray analysis in the transmission electron microscope (TEM).

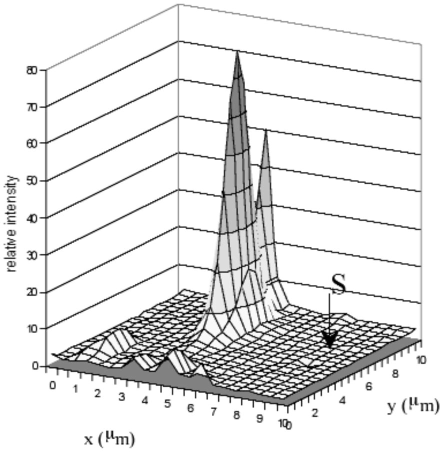

FIG. 1. Microbeam x-ray fluorescence scan of Fe, obtained from the examination of a TEM thin foil of Zircaloy-4, with a step size of 0.4 μm, showing the region where a point spectrum was measured.

We have conducted a study of alloying element concentrations in zirconium alloys using synchrotron radiation from the Advanced Photon Source (APS) at Argonne National Laboratory. The unique combination of spatial and elemental resolution of the microbeam line at the APS allows study of the alloying element concentrations at ppm levels in a region as small as 0.2 μm. We used x-ray fluorescence induced by this submicron x-ray beam to determine the concentration of these alloying elements in the matrix as a function of alloy type and thermal history.

Methods and Materials

We examined Zircaloy-4 samples obtained from the General Electric Corporation as plate material, and ZIRLO samples obtained from Westinghouse Electric Corporation in the form of tubing, as well as standards. The samples used in x-ray fluorescence experiments were standard TEM thin foils (about 100 nm thick in their thinnest region) prepared from strips of the alloys by mechanically grinding and electropolishing.

Results and Discussion

We performed microfluorescence examinations of the alloys by using a microfocused beam (on the 2ID-D/E beamlines) on the regions of interest to acquire point spectra. The beam size profile measured using a Cr knife-edge was determined to be 0.24 μm wide (FWHM). The acquisition times for such spectra were on the order of 600 s to 1500 s, which correspond to a vastly larger number of incident photons sampling the specimen than during a typical x-ray fluorescence experiment using a conventional x-ray tube source.

We used this microbeam to study the alloying element content in the zirconium matrix. Figure 1 shows the Fe fluorescence scan of a thin foil region of Zircaloy-4, taken on a 10 μm x 10 μm

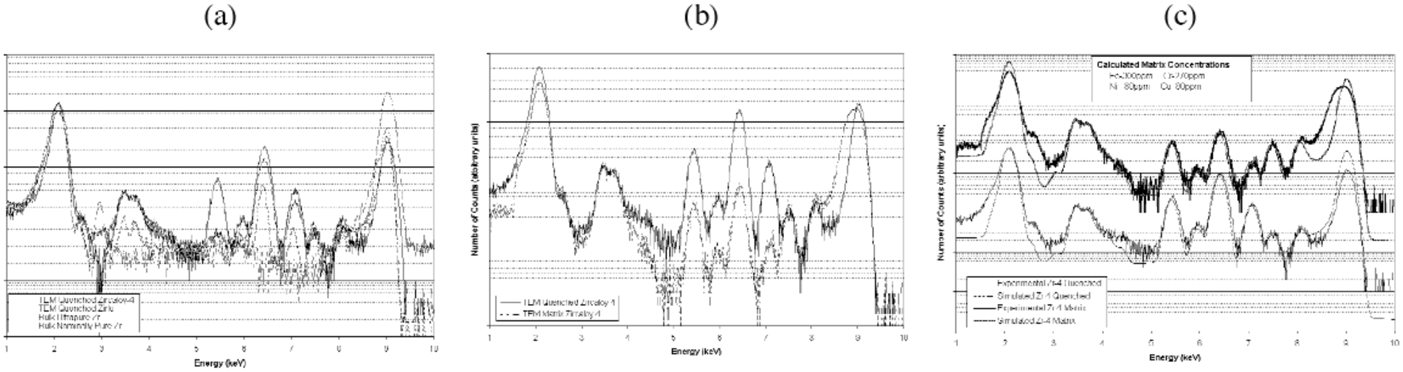

FIG. 2. Fluorescence spectra obtained from (a) quenched Zircaloy-4 TEM foil, quenched ZIRLO TEM foil and ultrapure Zr (bulk sample), and (b) quenched Zircaloy 4 TEM foil and the matrix region in a TEM foil of annealed Zircaloy-4. (c) X-ray intensity versus energy for quenched Zircaloy-4 and the matrix region of a fully recrystallized Zircaloy-4 TEM sample (solid lines) and MSIM5D Monte Carlo simulations (dashed lines), using the concentrations shown in the figure.

grid and a step size of 0.4 µm, showing the position of intermetallic precipitates. We then placed the beam on the region in between the precipitates and performed a more detailed scan of the smaller region (typically 2 by 2 µm, with a 0.1 µm step size and an acquisition time of 5 seconds per point) to ensure that no large variations of Fe content exist within those regions. We then positioned the beam in this lowest Fe region and acquired point spectra with the long acquisition times mentioned above. These spectra serve as the basis for our quantitative analysis of the matrix composition in those samples.

Figure 2a shows several fluorescence spectra acquired from four standards: (i) a TEM foil of a quenched Zircaloy-4 sample, (ii) a bulk sample of nominally pure zirconium, (ii) bulk ultrapure zirconium (acquired from Chalk River Laboratories), and (iv) from a TEM foil of quenched ZIRLO. As expected, the Fe peaks (between 6 and 7 keV) are highest for Zircaloy-4, next for ZIRLO, then nominally pure Zr and lastly ultrapure Zr. Figure 2b shows the same Zircaloy-4 quenched spectrum superimposed on the spectrum measured on a matrix spot of TEM foil made of fully recrystallized Zircaloy-4, clearly showing the lower Fe content in the matrix after precipitation.

To analyze the fluorescence spectra we used the MSIM5D program.[2] This Monte Carlo program simulates the interaction of an x-ray photon beam with a slab sample of arbitrary composition, explicitly taking into account the different scattering and fluorescence emission processes from both the material and from air. We simulated both the standards and the Zircaloy-4 matrix. Figure 2c (bottom) shows the measured and simulated spectra for quenched Zircaloy-4 (standard). The agreement with the measured bulk concentrations is excellent, giving confidence that the measurement and simulation techniques in combination can reproduce the standards quantitatively.

The quantitative analysis of the Zircaloy-4 matrix point spectra shown in Fig. 2c yielded the following concentrations: Sn: 1640 ppm, Fe: 300 wt ppm, Cr: 270 wt ppm. The matrix concentrations of Fe and Cr above are higher than the atom probe measurements performed in Zircaloy-2 by Kruger et al.,[3] who found a matrix value of ~ 140 wt ppm, and agree well with the atom probe measurements of Wadman et al.,[4] who found Fe concentrations in the Zircaloy-4 matrix between 230 and 380 wt ppm. If the current results are valid, this could mean that the actual concentration of alloying elements in the matrix is higher than the equilibrium concentration. These alloying elements may be in metastable equilibrium in the matrix, possibly associated with other alloying elements (such as O or Sn) and with lattice defects, such as dislocations and stacking faults.

Conclusions

Microbeam x-ray fluorescence measurements to study the alloying element content dissolved in solid solution in the matrix of Zircaloy-4 combined with Monte Carlo simulations yielded estimates of the alloying element content in the matrix of 300 wt ppm Fe and 270 ppm Cr. These concentrations will serve as the basic inputs of microstructural evolution models which depend on these concentrations to determine basic model parameters, such as atomic mobilities, the degree doping of zirconium oxides formed during waterside corrosion, or the source term for irradiation-induced precipitation. The fact that the concentrations are somewhat higher than expected may indicate that a metastable solution of these alloying elements exists in the matrix, which could help explain the different behavior of alloys suffering different heat treatments.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. This research was sponsored by the Department of Energy, Nuclear Engineering Education and Research (DOE-NEER) program, under grant number DE-FG07-98ID 13637.

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