Study of Second-phase Particles in Zirconium Alloys with X-ray Diffraction

S. Jurgensmeier,[1] A. Motta,[1] Y. Chu[2]
[1]Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA, U.S.A.
[2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Zirconium alloys are used extensively in the nuclear industry as cladding for nuclear fuel. The alloying content and distribution of second-phase particles change alloy performance. One way in which we can better understand the mechanisms by which these treatments affect alloy performance is to identify and quantify the second-phase particles in the alloys. However, the fraction of the second-phase particles is so small that greater x-ray intensity and resolution than are available from conventional x-ray sources need to be used.

By utilizing the facilities at APS, we are able to increase the resolution and precision of the data collected when compared with conventional sources. We have begun to quantify the fraction of second-phase particles in several alloys. We have also been able to identify additional phases present in other alloys. The results obtained are more accurate than those from previous examinations as a result of, in large part, the APS's capability for greater resolution. Such data will help in modeling the behavior of these alloys in service, as the specific roles of precipitates and alloying elements in solution can be distinguished.

Methods and Materials

In the last year, we have examined three different types of materials, organized in series (increasing heat treatment for same alloy, effect of cold work, and effect of alloy composition). We obtained intensity vs. 2θ for these alloys with a very small step size and enough statistics that we could perform Rietveld refinement on these spectra. The first set of materials was a combined series of Zircaloy-2 and Zircaloy-4 obtained from Westinghouse as bulk material. Eight samples were cut from each material, quenched, and heat treated so that the cumulative annealing parameter (CAP) varied from 10^{-19} to 10^{-17} h, with five annealing steps between the two extremes. The objective of this experiment was to discern the precipitation kinetics in that annealing range. The second set of materials examined was also provided by Westinghouse. It was a set of Zr-Nb-Sn-Fe alloys with treatments varying from a basic quench to being twice cold worked. This set was investigated in order to identify the effect of cold work on the formation of second-phase particles. The final set of samples, provided by Cezus of France, consisted of a series of model alloys with different combinations of alloying elements Fe, Cr, and Ni. This set was also examined qualitatively to identify the second phase and will later be quantified.

Results

The first set of Zircaloy-2 and Zircaloy-4 alloys was examined and analyzed according to the procedure developed in previous years to provide optimal data for statistical analysis through the Rietveld analysis program GSAS. Each sample was examined from 18° to 45° 2θ with a step size of 0.002°. Figure 1 shows an example of the current status of the fitting of one of these data spectra. The data and the fit are shown on the top line, and the residual is shown below. The high resolution allows for more accurate fitting of these spectra than in previous attempts. The material is consistent with our expectations, but complications have arisen in the texture of the material that have slowed analysis. We expect that by using increasing orders of spherical harmonics, we will be able to simulate the texture and get better quantitative values. Analysis of these spectra is ongoing.

The spectra obtained from the second set of samples, consisting of four Zr-Nb-Se-Fe alloys from Westinghouse, are shown in Fig. 2. In this figure, the second-phase peaks are located to the right of the first three large peaks. It is apparent from visual investigation

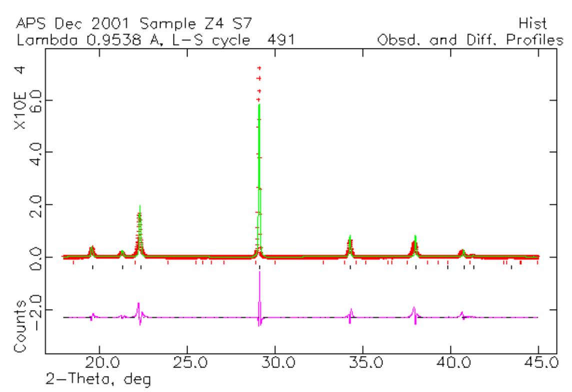

FIG. 1. Current status of Rietveld refinement of of Zircaloy-4 sample, CAP = 10^{-17} h. Calculated volume fraction of $Zr(Cr,Fe)_2$ second phase is about 0.4%.

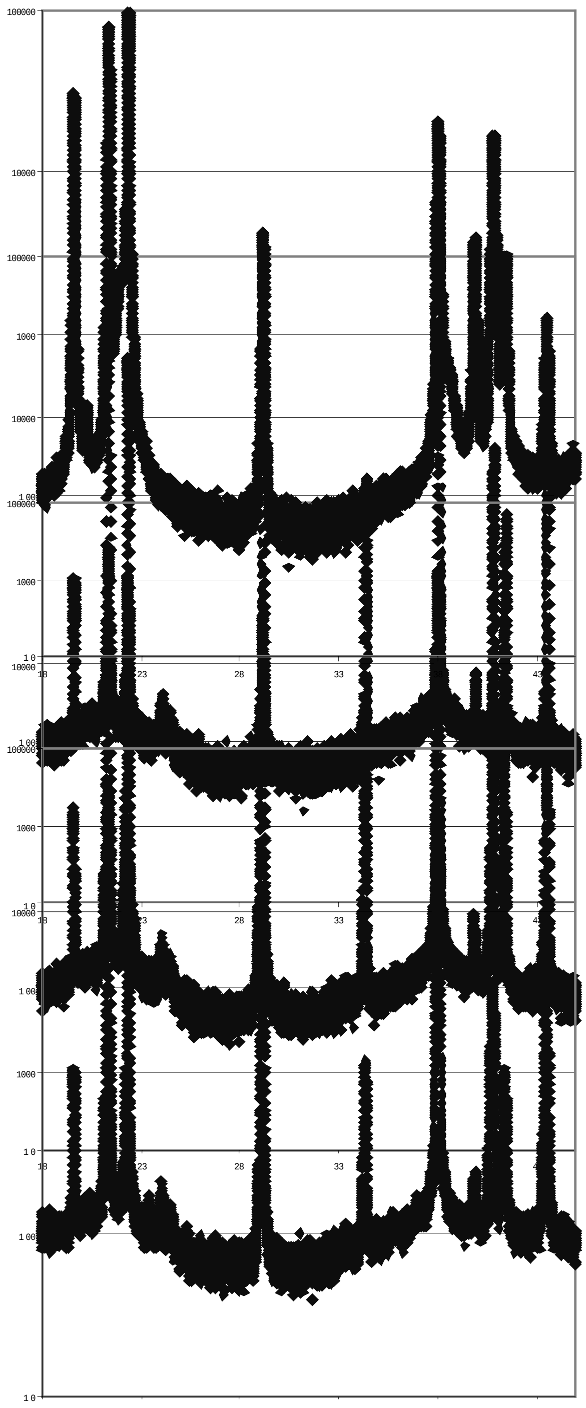

FIG. 2. Zr-Nb-Sn-Fe alloy series. The amount of cold work increases down the page.

that the peak height increases as the amount of cold work increases. (In the graph, the percent of cold work increases as the graphs descend.)

The third set of samples (model alloys) has been analyzed by peak location to determine which second phases are present. We found the expected second phases and some additional unidentified peaks, suggesting previously unreported phases resulting from a unique combination of alloying elements and heat treatment. Further analysis of these spectra is ongoing and will help provide more information about the development of these second phases with the variation of alloying elements.

Discussion

From the data collected, we have a much clearer picture of which second phases develop with heat treatment, and at what rate this development occurs. The Zircaloy-2 and Zircaloy-4 series have provided quantitative data to demonstrate the development of second-phase particles as heat treatment increases. The other samples have qualitatively shown the increase in second- phase particle growth with increased cold work and increased alloying elemental content. With further analysis, more quantitative data can be extracted from these spectra and provide more stringent standards upon which to base the creation of future alloys.

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