X-ray Diffraction Study of Second-Phase Particles in Zirconium Alloys

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Introduction

The structure and morphology of second-phase precipitates in Zr alloys used for nuclear fuel cladding of Zr alloys have been linked to several in-reactor degradation processes.[1] Understanding these links mechanistically requires direct measurement of the structure and volume fraction of these precipitates in the bulk alloy for particular thermomechanical treatments. However, the volume fraction of these precipitates is sufficiently small as to preclude the use of standard methods of phase determination using conventional x-ray generators.

We have conducted an x-ray diffraction study of second-phase particles in zirconium alloys using synchrotron radiation from the Advanced Photon Source (APS) at Argonne National Laboratory. The higher flux and angular resolution of the synchrotron radiation, compared to conventional x-ray generators, enables the detection of very small precipitate volume fractions. We have identified the crystal structure of second-phase precipitates, as the stable second phase (C14 hcp $Zr(Cr,Fe)_2$ precipitates) in Zircaloy-4. These precipitates were detectable at very early stages in the heat treatment process. We studied precipitation kinetics as a function of the cumulative annealing parameter (CAP) in the range 10^{-22} (quench) to 10^{-16} h and used these results to calculate precipitate volume fractions and average precipitate sizes at each annealing condition.

Methods and Materials

We examined Zircaloy-4 and Zircaloy-2 samples obtained from the General Electric Corporation as plate material. Samples suitable for x-ray diffraction were cut from the plate and annealed in a quartz tube filled with ultrahigh purity Ar for ten minutes at 1170K then quenched in water. After quenching, the samples were resealed into quartz tubes and annealed to various CAP[2] defined as $CAP=\sum_i t_i \exp(-Q/RT_i)$, where t_i is the time spent at temperature T_i and Q/R=40,000K. We used synchrotron radiation to examine a series of Zircaloy-2 and Zircaloy-4 samples in the quenched state and after annealing up to CAP=10^{-16} h.

Results

Figure 1 shows a series of x-ray diffraction pattern (intensity vs. two-theta angle) for Zircaloy-4 at different stages of heat treatment. We can index the peaks in the Zircaloy-4 spectrum as corresponding either to the α-Zr hcp phase or the C14 $Zr(Cr,Fe)_2$ hcp Laves phase ($MgZn_2$-type). The lattice parameters determined from the fit of the data correspond very well to the powder diffraction files for C14 hcp $Zr(Cr,Fe)_2$ (JCPDF File # 42-1289).[3]

We analyzed these x-ray patterns using the Rietveld method, as implemented in the GSAS program.[4] For the Zircaloy-4 annealing experiment, we calculated the precipitate volume fraction from the GSAS fit of the data. Figure 2a shows the precipitate volume fraction F as a function of CAP, normalized to the meas-

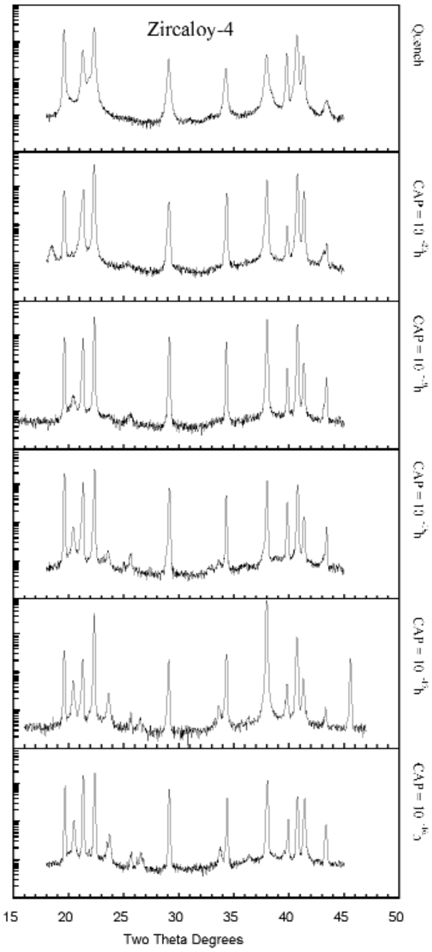

FIG. 1. Powder x-ray diffraction spectra of Zircaloy-4 obtained on a series of samples with increasing cumulative annealing parameter (CAP); the second phases (located near 23 and 25 degrees two-theta) increase and sharpen, as the CAP increases.

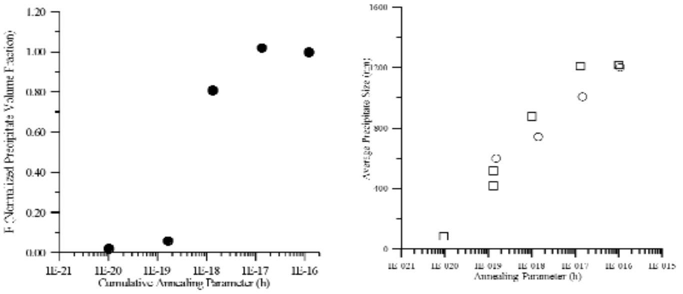

FIG. 2. (a) Normalized precipitate volume fraction versus annealing parameter (CAP) for Zr(Cr,Fe)2 precipitates in Zircaloy-4; (b) average particle size versus annealing parameter as measured by diffraction line broadening.

ured precipitate volume fraction at CAP=10^{-16} h as calculated from the measurements. The precipitate volume fraction increases with increasing annealing parameter, showing an S-shape. The data show that most of the precipitation occurs between 10^{-19} h and 10^{-18} h.

We also used the data to estimate the size of the precipitates from the line broadening of the precipitate peaks associated with particle size. The particle size d is given by the Scherrer equation: $d=0.9\lambda/B_\theta \cos\theta$, where $B_\theta=(B^2-B_i^2)^{1/2}$ is the particle size broadening for peak θ, B is the measured peak broadening (full-width half maximum, FWHM), B_i is the instrumental broadening measured using a standard, θ is the diffraction angle, and λ is the wavelength of the synchrotron radiation. The particle sizes are plotted in Fig. 2b against the log of the CAP. It is clear that the particle size increases continuously until 10^{-17} h and remains constant up to 10^{-16} h. The range of average particle sizes calculated here is somewhat smaller than the particle size determined previously in TEM examinations of these samples, at equivalent values of CAP. It is possible that artificially large average precipitate sizes are reported in TEM studies,[2] because the small size tail of the precipitate size distribution may evade detection in the TEM.

Conclusions

These results demonstrate that x-ray diffraction performed at the synchrotron radiation can provide detailed quantitative structural data about second-phase particles in Zr alloys, from very early stages in the thermal aging process. By calculating the average precipitate size and precipitate volume fraction in the bulk material, we can provide a firmer mechanistic basis for alloy design based upon achieving precise precipitate microstructures that are more resistant to in-reactor degradation.

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