

Hydrogen Precipitation Kinetics Measurement in Zircaloy-4 Using Synchrotron Irradiation X-Ray Diffraction

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INTRODUCTION

During normal operation of light water reactors, the zirconium alloy fuel cladding reacts with the oxygen of the water, creating a protective oxide layer (ZrO_2) and releasing hydrogen gas. Part of released hydrogen can enter the cladding material where it can diffuse driven by concentration and temperature gradients [1] according to:

$$J = -D\nabla C_{SS} - \frac{DQ^*C_{SS}}{RT^2}\nabla T \quad (1)$$

where D is the diffusion coefficient of hydrogen in zirconium, C_{SS} is the hydrogen content in solid solution, Q^* is the heat of transport, R the ideal gas constant and T the temperature. Only a certain amount of hydrogen can be accommodated in solid solution by the zirconium matrix. If the amount of hydrogen surpasses that limit, zirconium hydrides (ZrH_x) will form. This onset of the precipitation is governed by the terminal solid solubility for precipitation (TSS_p) [2]–[4].

Hydrogen precipitation decreases the hydrogen content in solid solution. An incorrect prediction of the hydrogen precipitation kinetics could lead to a miscalculation of the hydrogen distribution in the cladding. This in turn would make it difficult to predict material behavior in service.

The hydride precipitation kinetics have been previously described by Marino [5] as:

$$\frac{dC_{SS}}{dt} = -\alpha^2(C_{SS} - C_{eq}) \quad (2)$$

where C_{ss} is the hydrogen content in solid solution, α^2 is the growth kinetics parameter and C_{eq} is the solubility limit of hydrogen at the temperature of interest. In measuring α^2 previous authors equated $C_{eq}=TSS_p$ whereas recent data indicate that the true thermodynamic equilibrium is expressed by TSS_D and that TSS_p is a kinetic limit [6] as shown in Figure 1. Therefore, the value of α^2 measured in previous studies [7], [8] needs to be re-evaluated using the actual solubility limit, TSS_D .

EXPERIMENTAL METHODS

A first attempt at recalculating the kinetic parameter α^2 with the revised assumptions discussed above is presented here,

using the data obtained by Courty et. al. [8]. In this study three recrystallized Zircaloy-4 samples were used. The samples were etched in a solution of 1 part hydrofluoric acid, 10 parts nitric acid and 10 parts deionized water, to remove the native oxide. A layer of nickel was then deposited to prevent further oxidation of the material. The samples were then charged with hydrogen, using gaseous charging. Using Vacuum Hot Extraction, the hydrogen content was measured to be 400, 541 and 603 wt.ppm for the samples used in the study.

The samples were brought to Argonne National Laboratory for synchrotron radiation X-ray diffraction analysis at the Advanced Photon Source 1-ID beamline [8]. In the beamline, the sample can be heated up using an infra-red furnace while the synchrotron beam traverses the sample, providing X-ray diffraction information at a given time and temperature. During the experiments the samples were heated to a temperature high enough that the (111) delta hydride diffraction peak disappeared (535°C , $TSS_D=575$ wt.ppm [2]), indicating that hydrides were fully dissolved in the sample. The samples were then cooled down at a fast rate ($100^\circ\text{C}/\text{min}$) to achieve hydrogen supersaturation in solution and observe hydride precipitation during 120 minute holds at a series of target temperatures. Following the reaction kinetics during each hold at temperature permitted the determination of the value of α^2 at that temperature.

Figure 1 shows the measured hydrogen in solid solution (calculated from the total hydrogen content from which the precipitated hydrogen content estimated from the height of 111 diffraction peak is subtracted) during one of the experimental runs made at the Advanced Photon Source. The example given here was obtained during a hold at a temperature of 380°C . Figure 1 shows that as the temperature decreases, the hydrogen content in solid solution remains close to TSS_p . When the target temperature is reached and the temperature is held (see Fig.1), the hydrogen content continues to decrease, reaching below the TSS_p . After 120 minutes, the hydrogen content in solid solution is only 50 wt.ppm away from and approaching TSS_D . The fact that precipitation occurs below TSS_p during long holds suggests that TSS_p is a kinetic limit and that the thermodynamic solubility is TSS_D .

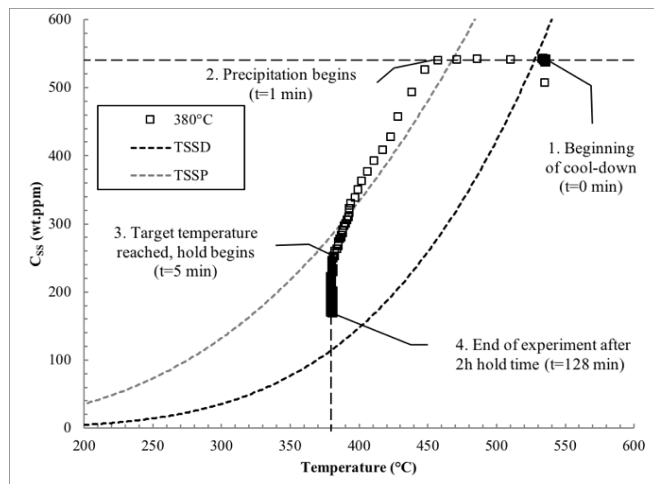


Fig. 1. Hydrogen content in solid solution versus temperature from [6], obtained from O. Courty et. al.'s diffraction data [8] of the sample containing 541 wt.ppm. More explanation can be found in [6]. The TSS_P and TSS_D curves are from Zanellato [7].

As a result, by using TSS_P as the equilibrium value, a bias in the measurement was introduced. The calculations of α^2 were therefore revised using $C_{eq}=TSS_D$ in equation (2).

RESULTS AND DISCUSSION

Calculations were performed in a similar way as done by Courty et al. [8], equation (2) was integrated and the experimental data was fitted using a MATLAB script for each sample and each temperature. The fits obtained were plotted in Figure 2. The α^2 values are found to be scattered between $4.2 \times 10^{-6} \text{ s}^{-1}$ and $1.3 \times 10^{-4} \text{ s}^{-1}$, which is one order of magnitude lower than what was observed by Kammenzind [7]. Courty et. al. [8] had found values of α^2 scattered between $3.7 \times 10^{-4} \text{ s}^{-1}$ and $5.2 \times 10^{-4} \text{ s}^{-1}$ which is also significantly higher. Such a change in values was expected, considering that TSS_P is significantly lower than TSS_D at the temperatures studied (a difference of 87 wt.ppm is observed at 288°C and 187 wt.ppm at 400°C between these two values of solubility) and therefore the driving force using TSS_D is higher than using TSS_P as the equilibrium solubility. The values of α^2 are seen to be scattered over two orders of magnitude and show little consistent trends. The scatter in the results indicates that the Marino hydrogen precipitation model reflected in equation 1 may not be applicable to hydride precipitation in Zircaloy. Using more sophisticated precipitation models such as the Johnson-Mehl-Avrami model [9] or the Sestak-Berggren model [10], might yield better results.

CONCLUSION

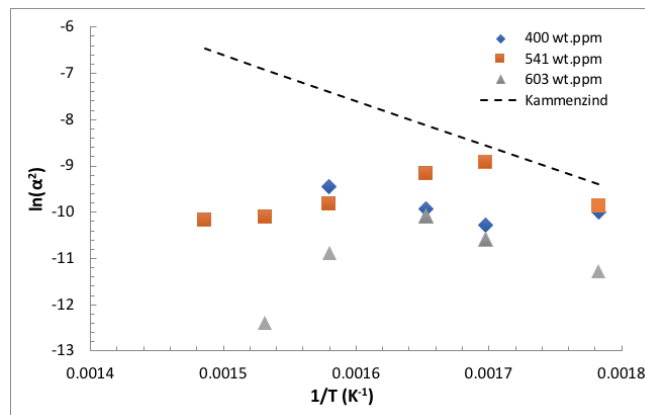


Fig. 2. Plot of the kinetics parameter α^2 presented by Marino[5], versus temperature measured using Courty et. al.'s data [8], and compared to results obtained by Kammenzind [7].

While previous authors used the terminal solid solubility for precipitation to calculate hydrogen precipitation kinetics, the results here show that TSS_D should be used as the equilibrium value. The measurement of α^2 performed by Courty et. al. in [8] was therefore revised using TSS_D as the solubility limit as was presented in this study. This revision of the data done for 13 different experiments performed on 3 different samples shows that hydride precipitation consistently continued past TSS_P and towards TSS_D . The recalculation of the α^2 parameter shows a wide scatter of values between $4.2 \times 10^{-6} \text{ s}^{-1}$ and $1.3 \times 10^{-4} \text{ s}^{-1}$ suggesting that the Marino model is not applicable to hydride precipitation. Improving the hydride precipitation model used should produce results that better agree with experiment.

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