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Dynamic mechanical analysis of hydrided and Un-hydrided Zr and Zircaloy-2

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Dynamic Mechanical Analysis of Hydrided and Un-hydrided Zr and Zircaloy-2

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Daniel Reese Lutz

May 1995

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Abstract

Dynamic Mechanical Analysis of Hydrided and Un-hydrided Zr and Zircaloy-2

by Daniel Reese Lutz

Understanding the mechanism of preferential hydriding in zirconium lined Zircaloy-2 fuel cladding requires knowledge of the temperature at which zirconium hydrides precipitate in zirconium and Zircaloy-2 during cooling. Other investigators have shown that internal friction and modulus variations are effective hydride precipitation indicators in Zr and Zr alloys. Dynamic mechanical analysis was used to measure these properties in polycrystalline Zr and Zircaloy-2 containing approximately 130 ppm and 20 ppm hydrogen during cooling from 475°C. Internal friction peaks and modulus inflections were observed in both hydrided and un-hydrided Zr and Zircaloy-2 at temperatures consistent with hydride precipitation temperatures. However, the onset of hydride precipitation could not be directly correlated to any of the observed internal friction peaks or modulus anomalies.

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1. Introduction

1.1 Background

Zirconium and zirconium alloys are key elements in nuclear reactors. Zirconium alloys are fabricated into fuel cladding, fuel spacers and fuel channels. Common alloys used are Zircaloy-2 (Zr-2), Zircaloy-4 (Zr-4), and Zr-2.5Nb. The approximate alloying content by weight of Zr-2 is 1.3% Sn, 0.17% Fe, 0.11% Cr, 0.05% Ni, and 0.12% O. Zr-4 is similar to Zr-2 with the exception of Ni which is present in only trace amounts. Zirconium is used as a thin lining, or barrier, on the inner surface of Zr-2 fuel cladding. The Zr liner is relatively pure with less than 0.05% Fe and 0.05% O.

The outer surface of the Zircaloy fuel cladding is in contact with steam at approximately 288°C and 1000 psig. This environment oxidizes the cladding according to the following reaction:

A portion of this hydrogen is absorbed into the cladding. Zirconium hydrides form when the solubility limit of hydrogen in the zirconium matrix is exceeded⁽¹⁾ as shown by the zirconium-hydrogen phase diagram in Figure 1. In most normal operating conditions fuel cladding will contain less than 200-300 ppm hydrogen after service life. However, in abnormal conditions several thousand ppm hydrogen can exist. Hydrogen is of concern mainly because of its embrittling effect in the form of precipitated zirconium hydrides⁽¹⁾.

Figure 1. The zirconium-hydrogen phase diagram¹.

Zirconium lined Zircaloy-2 cladding containing hydrogen that is cooled at a relatively slow rate from a temperature above the hydride solvus develops hydrides preferentially in the Zr liner. An example of this is shown in Figure 2 for Zr lined cladding specimens containing 550 ppm hydrogen that were cooled from 520°C at 20°C/s (Fig. 2a) or 0.07°C/s (Fig. 2b). When the specimen is fast-cooled (Fig. 2a), a distribution of zirconium hydrides develops that is similar in both the Zr and Zr-2. A small hydride free zone in the Zr-2 adjacent to the Zr interface exists. When the specimen is slow-cooled a different hydride distribution develops. The Zr liner becomes heavily hydrided throughout and bands of circumferential hydrides develop in the outer portion of the Zr-2 (Fig. 2b). The bulk of the Zr-2 contains small hydrides that precipitated some time after the circumferential hydrides formed.

The Zr-2 region that is devoid of the circumferential hydrides that developed during cooling is termed the "hydride free zone" (HFZ). This zone is either depleted of hydrogen or it is free of nucleation sites that would promote the formation of hydrides. The hydrides that would normally be present in the Zr-2 HFZ seem to be in the Zr liner and thus the liner has become preferentially hydrided. It is not known what the effect of a preferentially hydrided liner will have on in-reactor fuel performance, but it is thought that any condition that concentrates zirconium hydrides will be detrimental in that it may lead to embrittlement.

Figure 2. Preferential hydriding of a zirconium-lined Zircaloy-2 fuel cladding. For 550 ppm hydrogen specimens (a) cooled from 540°C at 20°C/s and (b) was cooled at 0.02°C/s. The slow cool promotes the formation of preferential hydriding in the Zr liner and a hydride free zone (HFZ) in the Zr-2.

The development of the HFZ could be explained by the following sequence of events during cooling from above the hydride solvus. First, hydrides nucleate in the Zr liner. The Zr-2 then acts as a hydrogen source for growth of the Zr liner hydride during continued cooling. This growth depletes the hydrogen in the Zr-2 adjacent to the Zr/Zr-2 interface. At some lower temperature, hydrides nucleate in the Zr-2. This temperature is dependent on the hydrogen concentration which is lowest near the Zr/Zr-2 interface because hydrogen has been depleted there. Because there is a gradient in the hydrogen concentration in the Zr-2, there is a gradient in the temperature at which hydrides nucleate in the Zr-2. Thus further cooling is followed by hydride nucleation and growth in the Zr-2 from the outer surface to the inner surface. This nucleation gradient results in large hydrides near the Zr-2 outer surface that nucleate early in the cooling and small hydrides that nucleate in the later stages of cooling.

There are two simple mechanisms that could cause precipitation first in the Zr. The first mechanism is based on hydrogen solubility effects and the second is based on undercooling effects. These two mechanisms are discussed below.

If the hydrogen solubility were lower in Zr compared to Zr-2 then hydrides would nucleate preferentially in the Zr. However, this mechanism is not plausible when the Zr and Zr-2 hydrogen solubility data of Kearns et al are compared⁽²⁾. These data, illustrated in Figure 3, show that there is only a small hydrogen solubility difference between Zr and

Figure 3. Kearns et al's hydrogen solvus in alpha zirconium and Zircaloy-2 determined by diffusion equilibrium⁽²⁾.

Zr-2. According to Kearns et al, hydrides should form in Zr and Zr-2 at essentially the same temperature during near-equilibrium cooling.

Selective precipitation in Zr vs. Zr-2 could be explained with a kinetic argument if the undercooling required to nucleate hydrides were different in Zr-2 compared to Zr. Consider the schematic time-temperature curves for hydride formation in Zr and Zr-2 shown in Figure 4. Hydrides form during cooling (from above the Zr and Zr-2 hydride solvus) when the time and temperature is reached that corresponds to the start of the hydride transformation process. Significant undercooling effects do exist in Zr and Zr-2. For example, Slattery⁽³⁾ measured the hydrogen solubility in Zr-2 by dilatometry during heating and cooling (Fig. 5). For 130 ppm hydrogen, the solvus temperature determined by heating is 359°C but during cooling it is found to be 279°C, an undercooling of 80°C. Erickson et al⁽⁴⁾ have shown a similar effect for Zr also using dilatometric measurements (Figure 5). It may be then that the formation of the HFZ shown in Figure 2 is not controlled by the equilibrium hydrogen solubility in Zr and Zr-2, but by the relative difference in undercooling required to nucleate zirconium hydrides in Zr and Zr-2.

What has been lacking in the consideration of hydride formation in Zr lined Zr-2 fuel cladding is a controlled study comparing the undercooling required to nucleate hydrides in Zr and Zr-2 under identical experimental conditions. It is the objective of this investigation to perform this comparative undercooling study and to shed light on the formation of the HFZ and preferentially hydrided Zr liner.

Figure 4. Schematic time-temperature curves showing possible undercooling differences in Zr and Zr-2. During cooling, zirconium hydrides will nucleate in Zr before Zr-2. Zr lined Zircaloy fuel cladding may develop a preferentially hydrided liner and a hydride free zone in the Zr-2 by this mechanism.

Figure 5. Hydrogen solubility in Zr and Zr-2 as determined by dilatometry showing supersaturation effects required to nucleate hydrides during cooling^(3,4).

1.2 Research Hypothesis

Under certain cooling conditions, zirconium lined Zircaloy-2 fuel cladding containing hydrogen develops zirconium hydrides preferentially in the zirconium liner. This concentrating effect is accompanied by a depletion of zirconium hydrides in the Zircaloy-2 and forms a hydride free zone. The development of the preferentially hydrided zirconium liner and the subsequent hydride free zone in the Zircaloy-2 would be explained if the amount of undercooling required to nucleate zirconium hydrides in zirconium is less than for Zircaloy-2. It is hypothesized that the development of the preferentially hydrided zirconium liner and the subsequent hydride free zone in the Zircaloy-2 is controlled by undercooling effects and the amount of undercooling required to nucleate zirconium hydrides in zirconium is less than for Zircaloy-2.

2. Principles of Dynamic Mechanical Analysis

2.1 Viscoelastic Behavior of Engineering Materials

Materials subjected to cyclic loading absorb energy, some of which may be stored elastically as potential energy and some of which is dissipated as heat. The mechanism of energy dissipation in materials is considered to be internal friction. Internal friction is a result of frequency/time dependent phenomena such as grain boundary sliding⁽⁵⁾ or diffusion of atoms from one interstitial site to another, as in the Snoek effect⁽⁵⁾.

Viscoelastic models have been developed to explain the observed phenomena of internal friction in materials^(5,6). The term “viscoelastic” is used to describe materials whose properties combine features of purely elastic solids and viscous liquids.

The elastic component in response to an applied load is best described in terms of a spring in which all energy during deflection is stored and can be regained by releasing the stress. The modulus relationship for such a system is described by the linear slope of the stress-strain plot shown in Figure 6.

The viscous component is analogous to a dashpot, which resists stretching with a stress that is proportional to the strain rate. The slope of the stress vs. strain rate curve is defined as viscosity as shown in Figure 7. The deflection energy in a dashpot is dissipated and cannot be recovered and is analogous to internal friction in a material.

A simple viscoelastic model consisting of two elastic components and a dashpot is shown in Figure 8. This model approximates the behavior observed in real materials. Consider a sinusoidal stress applied to this system such that

$$\sigma(t) = \sigma_a \sin(\omega t) \quad (2)$$

where σ_a is the stress amplitude and ω the angular frequency. The strain response of the model at any frequency is sinusoidal, but there is a phase shift, as specified by a phase angle δ , relative to the sine wave of the stress so that

$$\varepsilon(t) = \varepsilon_a \sin(\omega t - \delta) \quad (3)$$

Figure 6. Stress-strain response of an elastic spring element.

Figure 7. Stress response of a viscous element.

Figure 8. Simple viscoelastic model consisting of two elastic components and a dashpot. This configuration models the transient creep plus elastic behavior observed in materials⁶.

where ϵ_a is the strain amplitude. The two equations above are the parametric equations for an ellipse. Thus, the stress-strain response forms an elliptical hysteresis loop. The area inside this loop is a measure of the energy dissipated in each cycle.

If the stress is resolved into components both in phase (σ') and 90 degrees out of phase (σ'') with the strain then

$$\sigma' = \sigma_a \cos(\delta) \text{ in phase component} \quad (4)$$

$$\sigma'' = \sigma_a \sin(\delta) \quad 90^\circ \text{ out of phase component} \quad (5)$$

The corresponding in-phase (E') and out-of-phase moduli (E'') are determined directly from these last two equations when they are divided by ϵ_a ,

$$E' = \sigma' / \epsilon' = (\sigma_a / \epsilon_a) \cos(\delta) = E^* \cos(\delta) \quad (6)$$

and

$$E'' = \sigma'' / \epsilon'' = (\sigma_a / \epsilon_a) \sin(\delta) = E^* \sin(\delta) \quad (7)$$

where E^* is the absolute modulus given by $\{E'^2 + E''^2\}^{1/2}$. E' reflects the elastic response of the material, since the stress and strain components are in phase. This part of the strain energy, introduced to the system by the application of the stress σ_a , is stored but then completely released when σ_a is removed. Consequently, E' is called the storage modulus. E'' describes the strain energy that is completely dissipated and is thus called the loss

modulus. The relative amount of damping or energy loss in the material is given by the loss tangent, or internal friction, where

$$\tan(\delta) = (E'' \sin(\delta)) / (E' \cos(\delta)) = E''/E' = Q^{-1} \quad (8)$$

A material that exhibits large damping will have a large lag between the applied stress and the strain and subsequently will have a large Q^{-1} .

The internal friction exhibits a maxima when plotted versus angular frequency ω as shown in Figure 9. At frequencies high compared to the resonant frequency, ω_d , the dashpot is essentially rigid. Deflection is thus prevented in spring E_2 (see Fig. 8) and occurs only in E_1 , so that the response is essentially linear with stiffness E_1 . Conversely, at frequencies low compared to ω_d , there is sufficient time for free movement of the dashpot, so that it has little effect. The elliptical loop again reduces to a straight line, but in this case with the lower stiffness E_c corresponding to E_1 and E_2 in series where

$$E_c = (E_1 E_2) / (E_1 + E_2) \quad (9)$$

The elastic modulus thus varies with frequency, increasing from E_c at low frequency to E_1 at high frequency (see Fig. 9). The transition between the two, i.e., the elliptical hysteresis response of Figure 9a, occurs in the region of the energy dissipation peak where $\omega/\omega_d = 1$.

(a)

(b)

Figure 9. Behavior of a viscoelastic model consisting of transient creep and elastic elements⁽²⁾.
 (a) Elliptical stress-strain response. (b) Variation of modulus and Tan delta with frequency.

The variation of the ratio E^*/E_1 with the normalized frequency ω/ω_d is shown in Figure 9b for the simple viscoelastic model that has just been described. It is clear that a significant variation in modulus can occur in the vicinity of an internal friction peak.

2.2 Viscoelastic Behavior of Hydrogen Bearing Zr and V Alloys

The onset of hydride precipitation during cooling has been detected in Zr, Zr alloys, and in V by variations in internal friction and elastic modulus⁽⁷⁻⁹⁾. Some key observations from these works will be discussed next.

Ritchie et al^(7,8) have observed an internal friction hydride precipitation peak during continuous cooling of high purity Zr as shown in Figure 10a. Ritchie et al's precipitation peak is truncated on the high temperature side and appeared at lower temperatures as the hydrogen content was decreased to very low hydrogen levels (9 ppm). Also shown in Figure 10a is the internal friction spectrum during heating. There is a hysteresis in the heating and cooling curves. As shown in Figure 10b, the internal friction hydride precipitation peak correlates with a marked increase in the square of the resonant frequency, f^2 , which is proportional to the elastic modulus⁽¹⁰⁾. An internal friction hydride precipitation peak was not observed however for Zr-2.5Nb⁽⁸⁾ even though there is a marked change in modulus (Fig. 11). The change in dynamic modulus is correlated with hydride precipitation.

(a)

(b)

Figure 10. (a) Hydride internal friction precipitation peak in 99.999% pure polycrystalline zirconium containing 200 ppm hydrogen⁽⁸⁾. (b) Frequency inflection correlating to the internal friction peak. The square of the frequency is proportional to the modulus. The data was collected during cooling at $1^{\circ}\text{C}/\text{min}$ under resonant frequency conditions. The peak occurs at about 2 Hz.

Figure 11. (a) Absence of internal friction hydride precipitation peak in Zr-2.5Nb containing 200 ppm hydrogen. (b) Although the internal friction peak was not observed, an inflection in the resonant frequency (which is proportional to the modulus) was correlated to hydride precipitation⁽⁸⁾.

Owen et al⁽⁹⁾ identified an internal friction hydride precipitation peak in vanadium-hydrogen alloys. The precipitation peak shown in Figure 12 was similar to that described by Ritchie et al in that it is truncated on the high temperature side. Variation of the oscillation frequency had an effect on the internal friction peak, but only after the onset of hydride precipitation. The precipitation indicator, however, was frequency independent (Figure 12).

One way of measuring the internal friction and modulus simultaneously is by dynamic mechanical analysis (DMA) whereby a thin rectangular section beam is subjected to sinusoidal, low amplitude deflection. DMA was therefore used in the current investigation to determine the undercooling required to nucleate zirconium hydrides in Zr and Zr-2.

3. Experimental

3.1 DMA Apparatus

The TA Instruments¹ Model 983 dynamic mechanical analyzer (DMA) tests materials for elasticity and viscous damping. In the DMA, materials are deformed in a sinusoidal, low-strain amplitude manner as shown in Figure 13. The two resulting measurements are storage modulus, which relates to the stiffness or elasticity of a

¹ TA Instruments, Wilmington, DE

Figure 12. Effect of oscillation frequency on hydride precipitation peak position for vanadium containing 145 ppm hydrogen. The precipitation indicator is independent of frequency⁽⁹⁾.

Figure 13. Deflection mode of rectangular specimen in the Model 983 dynamic mechanical analyzer.

material, and internal friction, which determines the material's viscous loss properties. Detailed equations for calculating the internal friction and storage modulus for the Model 983 DMA are contained in Appendix 1.

The Model 983 DMA system is composed of a drive assembly and a furnace that are interfaced to an IBM PS2 computer. The drive assembly contains an electromagnetic driver and a linear variable displacement transducer (LVDT) which are shown in Figure 14. The electromagnetic driver displaces and drives the specimen-arm system; the LVDT measures the arm position. A thermocouple located approximately 1 mm from the specimen senses the specimen temperature and transmits this information to the control electronics located in the DMA base.

When the drive arm is deflected slightly as the result of an electrical signal to the driver, the specimen is flexed. The loading is continued at a selected frequency using a sinusoidal driver signal that is fully reversed. The LVDT measurement is used to determine the phase angle. The magnitude of the driver signal required for a particular oscillatory amplitude is a measure of the specimen stiffness.

3.2 Materials

Specimens used in the DMA testing program were fabricated from a hollow zirconium lined Zircaloy-2 tubeshell. This tubeshell is a co-extrusion of Zr and Zr-2 with a 6.35 cm OD and 1.09 cm wall thickness. The outer portion comprises the Zr-2 and the inner portion comprises the Zr portion with a 0.19 cm thickness. The vendor ingot

Figure 14. TA Instruments Model 983 dynamic mechanical analyzer electromechanical system.

material certifications for this material are contained in Table 1 for the Zr-2 and in Table 2 for the Zr.

Table 1. Composition of Zircaloy-2 ingot UO2730LB used in DMA testing.

Sn	Fe	Cr	Ni	O	N	H
1.33	0.17	0.10	0.07	0.12	<40	<12

Note: Hydrogen and nitrogen are given in wppm while all other compositions are given in weight percent

Table 2. Composition of zirconium ingot used in DMA testing.

Sn	Fe	Cr	Ni	O	N	H
<50	150	<100	<35	377	<30	<12

Note: Compositions are given in wppm.

A longitudinal strip 1.27 cm wide was cut from the tubeshell, containing the Zr-2 and Zr portions. The strip was then machined into a flat bar approximately 0.38 cm thick, 0.95 cm wide and 18 cm long. The resulting bar contained the Zr-2/Zr interface, with each portion being approximately 0.19 cm thick.

A portion of this bar stock was set aside for hydrogen charging and a portion was set aside to remain un-hydrided. To hydride the materials, zirconium hydride chips ($\text{ZrH}_{1.9}$) were added to a pyrex tube containing the bar stock. The pyrex tube was evacuated to 30 mm Hg and backfilled to 5 psi with Ar. The evacuation and backfilling procedure was repeated 3 times. The pyrex tube was then sealed with an oxygen/methane torch under the 5 psi partial pressure of Ar. A similar procedure was done for the control bar stock, but without the hydride chips.

The bar stock was annealed in the pyrex tubing containing the hydride chips for 7 days at 650°C. At the end of the homogenization period the specimens were cooled to 250°C at a rate of approximately 0.07°C/s and then water quenched to room temperature.

The annealed materials were next sectioned along the mid-thickness plane (along the Zr/Zr-2 interface) with a 0.0076 cm kerf saw. At this point in the processing 4 sheets existed: an un-hydrided Zr control, an un-hydrided Zr-2 control, a hydrided Zr, and a hydrided Zr-2. Each of these sheets was then coldworked in a rolling mill to a nominal thickness of 0.076 cm and then recrystallized for two hours at 650°C in an open air box furnace to develop equiaxed grains. The purpose of the air anneal was to develop a surface oxide that would prevent the hydrogen from outgassing during the elevated temperature DMA testing.

Specimens were then cut from the sheets for DMA testing; the dimensions of these specimens are shown in Table 3. Two specimens for hydrogen determination were

Table 3. Final dimensions of specimens used for DMA testing.

Material	Length	Width	Thickness
	(mm)	(mm)	(mm)
Zr low hydrogen*	51.5	10.00	0.69
Zr high hydrogen*	50.9	9.41	0.72
Zr-2 low hydrogen*	51.1	10.00	0.68
Zr-2 high hydrogen*	50.5	9.70	0.76

** see Table 4 for hydrogen contents*

removed from the regions adjacent to where coupons were cut for the hydrided DMA specimens. A specimen for hydrogen determination was removed from the un-hydrided Zr and Zr-2 pre-DMA test specimens. These specimens were then analyzed for hydrogen by an inert gas fusion technique. The results of this analysis are shown in Table 4. The average hydrogen compositions are quite similar (126 and 128 ppm) while the un-hydrided specimens do indeed have a low hydrogen composition that is consistent with the vendor material certifications (compare Table 4 with Tables 1 and 2). As will be discussed in the results section, the DMA specimens did not outgas hydrogen during the DMA tests.

The purpose of hydriding sheet stock fabricated from the metallurgically bonded Zr and Zr-2 was to ensure a comparable hydrogen concentration between the Zr and Zr-2.

Table 4. Results of inert gas fusion analysis of hydrided and un-hydrided sheet stock adjacent to DMA specimens.

Material	Hydrogen Content Region 1 (ppm)	Hydrogen Content Region 2 (ppm)	Average Hydrogen Content (ppm)
Zr low hydrogen	15	N/A	N/A
Zr-2 low hydrogen	20	N/A	N/A
Zr high hydrogen	131	120	126
Zr-2 high hydrogen	121	135	128

Based on the hydrogen analyses this goal was achieved. However, specimens from other regions of the hydrided bar stock were analyzed for hydrogen and did vary in absolute hydrogen content. The results of these analyses gave 142 and 155 ppm hydrogen. This result shows that chemical homogeneity was not achieved on a macro scale. Because of this variability in hydrogen concentration from different regions of the stock material, it was decided to ensure comparable specimen to specimen hydrogen concentrations by using only one set of DMA specimens.

The microstructures of the DMA specimens are shown in Figures 15, 16, 17 and 18. The specimens exhibit equiaxed recrystallized grains. The grain size of the Zr is considerably larger than that of Zr-2 (ASTM 7 vs. 12, respectively). The relative difference in alloying elements between Zr and Zr-2 can be seen in the large number of intermetallic precipitates in the Zr-2.

Polarized Light 10 μm —

Brightfield 10 μm —

Figure 15. Microstructure of Zr 15 ppm DMA specimen prior to testing.

Figure 16. Microstructure of Zr 126 ppm DMA specimen prior to testing.

Polarized Light 10 μm —

Brightfield 10 μm —

Figure 17. Microstructure of Zr-2 20 ppm DMA specimen prior to testing.

Figure 18. Microstructure of Zr-2 128 ppm DMA specimen prior to testing.

3.3 DMA Test Parameters

3.3.1 Continuous Cooling

The continuous cooling DMA experiments tested the four material conditions: 15 and 126 ppm hydrogen Zr and 20 and 128 ppm Zr-2. The specimens were individually heated to 475°C and held for ten minutes. After the ten minute hold, the temperature was decreased to room temperature at a constant rate of 5°C/minute until room temperature. During cooling, the internal friction and storage modulus were determined at 3, 5, and 7 Hz at 1°C intervals. The oscillation amplitude for the DMA continuous cooling tests is 0.5 mm which corresponds to approximately 2×10^{-4} flexure strain and 5×10^{-3} shear strain.

3.3.2 Isothermal Hold

Only the Zr-2 130 ppm hydrogen specimen was used in the isothermal hold experiment. The specimen was heated to 400°C and held for 10 minutes and then cooled rapidly ($\sim 15^\circ\text{C}/\text{minute}$) to the isothermal hold temperature of 300, 325, 350, or 375°C. Once the ten minute soak period was completed, the internal friction and storage modulus were determined at 5 Hz at 30 second intervals for a total of about 110 minutes. The oscillation amplitude for the DMA isothermal hold test is 0.2 mm which corresponds to approximately 8×10^{-5} flexure strain and 2×10^{-3} shear strain.

4. Dynamic Mechanical Analysis Results

4.1 Continuous Cooling

The internal friction (Tan delta) and storage modulus were measured during cooling at a rate of 5°C/minute from 475°C at 3, 5, and 7 Hz. It is observed that Zr and Zr-2, hydrided and un-hydrided alike, exhibit anelastic behavior under these experimental conditions. A description of the DMA results is given below.

4.1.1 Zr 15 ppm Hydrogen

The temperature and frequency dependence of the Tan delta and storage modulus for the Zr 15 ppm hydrogen specimen is shown in Figure 19.

As summarized in Table 5, 6 internal friction peaks have been identified. One of these, ZR15-6, was so broad that an exact temperature could not be associated with the peak but it occurred at about 300°C. Some analysis can be made to determine if any of the peaks are associated with the same process. The resonant frequency of a given internal friction process has an Arrhenius type temperature dependence⁽⁵⁾. At a given temperature T the resonant frequency is given by

$$f = f_0 \exp(-\Delta H/RT) \quad (10)$$

Figure 19. Variation with temperature and frequency of Tan delta and storage modulus of Zr 15 ppm hydrogen specimen during cooling from 475°C at 5°C/s.

Table 5. Identification of internal friction peaks in Zr 15 ppm hydrogen DMA specimen during continuous cooling. (Reference Fig. 19)).

Peak #	Frequency (Hz)	Tan delta	Temperature (°C)
ZR15-1	5	0.054	205
ZR15-2	7	0.0125	245
ZR15-3	3	0.072	337
ZR15-4	5	0.11	402
ZR15-5	3	0.024	220
ZR15-6	7	0.01	~ 300 (not resolved)

where f is the resonant frequency at absolute temperature T . The process has an activation energy ΔH and pre-exponential constant f_0 . This model predicts that an increase in frequency will increase the temperature at which the peak is observed. This is easy to understand when one considers that atomic processes are more mobile at higher temperatures. The frequency required to resonate with a given process therefore increases.

If the resonant frequency is measured at two different temperatures then the activation energy is given by

$$\Delta H = R \ln(f_2/f_1)/(1/T_1 - 1/T_2) \quad (11)$$

where

T_1 = absolute temperature of internal friction peak at frequency f_1

T_2 = absolute temperature of internal friction peak at frequency f_2

$R = 8.312 \text{ J/mol-K}$

Based on this type of reasoning, peaks ZR15-1 and ZR15-2 are associated with the same process with an activation energy of 18 kJ/mol. Likewise, peaks ZR15-3 and ZR15-4 are associated with the same process an activation energy of 29 kJ/mol.

The expected 7 Hz peak associated with peaks ZR15-1 and ZR15-2 should appear at approximately 450°C, which did not occur. However, a small inflection in the internal friction did occur at 7 Hz near 425°C which may be the expected event.

The general features of the storage modulus are a very strong, non-linear increase in modulus with decreased temperature. The modulus decreases from approximately 95 GPa near room temperature to about 20 GPa at about 450°C. The modulus has inflections, some of which are easily correlated with internal friction peaks observed in the internal friction spectrum. However, the magnitude of the modulus inflection does not seem to be related to the internal friction peak height at the peak temperature. For example, a strong modulus transition occurs at about 400°C. This variation is about the same for the 5 and 7 Hz frequencies, but the internal friction in that temperature range are different by about a factor of six.

It is noteworthy that below 200°C the internal friction at all three frequencies is decreasing and approaching the same low value of about 0.01. This decrease in internal friction is accompanied by a decrease in the frequency dependence of the modulus, i.e., the moduli at all three frequencies approach the same value. If one assumes that the change in modulus is entirely due to the internal friction events, then this observation shows that internal friction processes have significant influences on modulus.

4.1.2 Zr 126 ppm Hydrogen

The temperature and frequency dependence of the Tan delta and storage modulus for the Zr 126 ppm hydrogen specimen is shown in Figure 20.

A series of internal friction peaks were observed that are summarized in Table 6. Although the internal friction spectrum of the Zr 15 and 126 ppm hydrogen specimens are different, they contain the same peaks with the exception of peak ZR126-3 which was not observed. Peaks ZR126-1 and ZR126-2 have an activation energy of 15 kJ/mol which compares very well with that of peaks ZR15-1 and ZR15-2.

Even though the same peaks exist in both specimens, they do not have the same peak height. For example, the ZR15-4 peak has a Tan delta of approximately 0.12 but is only about 0.04 for the ZR126-4 peak amid a very high background.

The storage modulus of the Zr 126 ppm hydrogen specimen had a frequency and temperature dependence similar to the Zr 15 ppm hydrogen specimen. The modulus

Figure 20. Variation with temperature and frequency of Tan delta and storage modulus of Zr 126 ppm hydrogen specimen during cooling from 475°C at 5°C/s.

Table 6. Identification of internal friction peaks in Zr 126 ppm hydrogen DMA specimen during continuous cooling. (Reference Fig. 20).

Peak #	Frequency (Hz)	Tan delta	Temperature (°C)
ZR126-1	5	0.036	200
ZR126-2	7	0.025	250
ZR126-3	3	not observed	not observed
ZR126-4	5	0.036	420
ZR126-5	3	0.015	230

decreases from approximately 95 GPa near room temperature to about 30 GPa at about 450°C and contains inflections in the modulus at various temperatures.

4.1.3 Zr-2 20 ppm Hydrogen

The temperature and frequency dependence of the Tan delta and storage modulus for the Zr-2 20 ppm hydrogen specimen is shown in Figure 21.

The internal friction spectrum for this Zr-2 specimen only contains 1 internal friction peak (ZR220-1) compared to the 4+ observed in the Zr. This 3 Hz internal friction peak centered about 400°C is very broad with a peak height of 0.018 (see Table 7). At 5 Hz the internal friction increases from about 0.01 to 0.03 between 400 and 450°C which

Figure 21. Variation with temperature and frequency of Tan delta and storage modulus of Zr-2 20 ppm hydrogen specimen during cooling from 475°C at 5°C/s.

Table 7. Identification of internal friction peaks in Zr-2 20 ppm hydrogen DMA specimen during continuous cooling. (Reference Fig. 21).

Peak #	Frequency (Hz)	Tan delta	Temperature (°C)
ZR220-1	3	0.018	400

suggests that a 5 Hz internal friction peak exists above this temperature the temperature range investigated.

The magnitude of the internal friction of this Zr-2 specimen is generally less than for the Zr specimens. For example the maximum Tan delta observed in the Zr spectrum was approximately 0.15 while the maximum Tan delta for the Zr-2 20 ppm hydrogen specimen is about 0.06. Chemistry and grain size effects could explain this. Tin and oxygen strengthen the matrix of the Zr-2 by solid solution strengthening effects while Fe, Cr, and Ni, which have a very low solubility in Zr, form intermetallic particles that are dispersed throughout the matrix. These factors appear to either pin the internal friction processes in Zr-2 or to stiffen the matrix and thus reduce its internal friction.

The temperature and frequency dependence of the Zr-2 storage modulus is much less than that of the Zr specimens. The modulus decreases from approximately 90 GPa near room temperature to about 45 GPa near 450°C. The modulus does not have many inflections which is consistent with the low internal friction. One particular modulus inflection occurs in the temperature range of about 250-300°C. This inflection is not

associated with an internal friction peak. It may be that the modulus is sensitive to internal friction events that are so weak that they are not observed. Alternatively, the observed modulus inflection may be a true variation in the elastic modulus that has not been influenced by internal friction processes.

The modulus measured at 3 Hz contains an unexplained feature in the temperature range of 250-300°C. During cooling there was a sharp drop in modulus of 2-3 GPa. The modulus eventually had a sharp rise of 2-3 GPa. A similar feature exists between about 150 and 200°C. The existence of these features is peculiar because they are not accompanied by a similar change in modulus at 5 or 7 Hz. In addition, there is not a corresponding change in the Tan delta. If the specimen slipped during the DMA test, then similar behavior would have been observed at the other frequencies and in the Tan delta data.

4.1.4 Zr-2 128 ppm Hydrogen

The temperature and frequency dependence of the Tan delta and storage modulus results for the Zr-2 128 ppm hydrogen specimen is shown in Figure 22.

The internal friction spectrum for this Zr-2 specimen contains 4 internal friction peaks as summarized in Table 8. The broad 3 Hz peak (ZR2126-1) observed in the Zr-2 20 ppm hydrogen (ZR220-1) specimen is not readily resolved because of the tail of the 3 Hz, 450°C internal friction peak (ZR2128-4). The 5 (ZR2128-2) Hz peak occurs at a

Figure 22. Variation with temperature and frequency of Tan delta and storage modulus of Zr-2 128 ppm hydrogen specimen during cooling from 475°C at 5°C/s.

Table 8. Identification of internal friction peaks in Zr-2 128 ppm hydrogen DMA specimen during continuous cooling. (Reference Fig. 22).

Peak #	Frequency (Hz)	Tan delta	Temperature (°C)
ZR2128-1	3	~ 0.015 (not resolved)	~ 400 (not resolved)
ZR2128-2	5	0.020	300
ZR2128-3	7	0.029	355
ZR2128-4	3	0.060	450

slightly lower temperature than the 7 (ZR2128-3) Hz peak. It is likely then that these two peaks are associated with the same internal friction process with an activation energy of 19 kJ/mol.

The storage modulus varies from approximately 95 GPa near room temperature to about 40 GPa near 450°C. An inflection in the modulus data occurs at about the same temperature (about 250-300°C) as that observed in the Zr-2 20 ppm hydrogen specimen.

4.1.5 Repeatability of DMA Test Results

The Zr 15 ppm hydrogen DMA test was performed twice to ascertain potential test to test variability. These repeat tests were performed several months apart using the same specimen and no other tests were performed on the specimen in between the two tests. Figure 23 shows the DMA results for this repeat test, while Figures 24, 25, and 26 test-

Figure 23. Variation with temperature and frequency of Tan delta and storage modulus of Zr 15 ppm hydrogen repeat specimen during cooling from 475°C at 5°C/s.

Figure 24. Repeatability comparison of Zr 15 ppm hydrogen DMA results during cooling from 475°C at 5°C/s and at 3 Hz.

Figure 25. Repeatability comparison of Zr 15 ppm hydrogen DMA results during cooling from 475°C at 5°C/s and at 5 Hz.

Figure 26. Repeatability comparison of Zr 15 ppm hydrogen DMA results during cooling from 475°C at 5°C/s and at 7 Hz.

provide a side-by-side comparison for each frequency. Seven internal friction peaks were identified and are summarized in Table 9. The characteristics of the internal friction peaks that developed in the two tests are compared in Table 10. It is clear that there can be test-to-test differences in modulus and Tan delta with the same specimen. The following observations are made:

- Internal friction peaks can change in magnitude by a few percent to more than one hundred percent. Internal friction peaks may appear or disappear on subsequent tests.
- Internal friction peaks can exhibit temperature shifts of a few degrees to at least 25°C.
- At a given temperature, the modulus can shift by as much as 20 GPa.
- Modulus inflections are not necessarily repeatable.

Table 9. Identification of internal friction peaks in second DMA test of Zr 15 ppm hydrogen specimen. (Reference Fig. 23).

Peak #	Frequency (Hz)	Tan delta	Temperature (°C)
ZR15'-1	5	0.052	190
ZR15'-2	7	0.027	270
ZR15'-3	3	not observed	not observed
ZR15'-4	5	0.190	430
ZR15'-5	3	0.025	230
ZR15'-6	7	0.020	295
ZR15'-7	5	0.032	285

Table 10. Comparison of internal friction peaks in Zr 15 ppm hydrogen specimen during continuous cooling from first and second tests.

Peak Comparison	Frequency (Hz)	Tan delta 1st test	Tan delta 2nd test	Temperature (°C) 1st test	Temperature (°C) 2nd test
ZR15-1/ZR15'-1	5	0.054	0.052	205	190
ZR15-2/ZR15'-2	7	0.0125	0.027	245	270
ZR15-3/ZR15'-3	3	0.072	not observed	337	not observed
ZR15-4/ZR15'-4	5	0.11	0.190	402	430
ZR15-5/ZR15'-5	3	0.024	0.025	220	230
ZR15-6/ZR15'-6	7	0.01	0.020	~ 300 (broad, not resolved)	295

4.2 Isothermal Quench and Hold

The Zr-2 128 ppm hydrogen specimen was solution treated at 400°C and then cooled to either 300, 325, 350, or 375°C and held for approximately 110 minutes while measuring the Tan delta and storage modulus. The cooling curves for these experiments are shown in Figure 27. It took at most 4 minutes for the specimens to cool to within a few degrees of the final hold temperature. Final equilibration took a few minutes more.

The internal friction and storage modulus results for the isothermal quench and hold experiment are shown in Figure 28. The storage modulus increases rapidly during the equilibration period but then approaches a steady state. The internal friction also

Figure 27. Cooling curves for isothermal quench and hold studies of internal friction processes in Zr-2 128 ppm hydrogen at 5 Hz.

Figure 28. Internal friction and storage moduli for isothermal quench and hold studies of Zr-2 128 ppm hydrogen at 5 Hz after rapidly cooling from 400°C.

increases rapidly during the equilibration period but decreases to a steady state, thus exhibiting a maximum.

The amount of time for the storage modulus and internal friction to reach a steady state is much longer than the time required to equilibrate the temperature. The initial changes probably have very little significance due to the rapidly changing temperature. The changes that occur after the specimens have equilibrated in temperature are indicative of a stabilization of the structure that reduces the internal friction in the specimens and thus increases the storage modulus.

The relative magnitudes of the moduli are not consistent with what one would predict based simply on the relative difference in temperatures. The highest temperature should correlate to the lowest modulus and the lowest temperature should correlate to the highest modulus. But this is not what is observed. In addition, the steady state moduli at a given temperature are not comparable to their counterparts from the continuous cooling experiments as shown in Table 11. Internal friction may be contributing to the observed modulus shifts. An internal friction process is expected to decrease the modulus as illustrated in Figure 9. This is consistent with the 350 and 375°C specimens. These two specimens do have the lowest moduli as expected based on temperature, but they also both have relatively large Tan deltas, with the 375°C specimen having the highest value. A similar argument can be made for the 300 and 325°C specimens. The 300°C specimen, which should have the largest modulus, has more internal friction than the 325°C

Table 11. Comparison of storage modulus and Tan delta from continuous cooling and isothermal 5 Hz DMA experiments at selected temperatures for Zr-2 128 ppm hydrogen.

Temperature (°C)	Continuous Cooling E'	Isothermal E' at 120 minutes	Continuous Cooling Tan δ	Isothermal Tan δ at 120 minutes
375	54	67	0.012	0.013
350	57	61	0.009	0.019
325	61	79	0.011	0.000
300	66	75	0.019	0.000

specimen and should cause a decrease in modulus. However, the internal friction at 300 and 325°C decays to approximately zero after about 40 minutes but the corresponding moduli do not reverse as might be expected if internal friction were the only factor controlling the modulus.

4.3 Post-Test Microstructure

Post-test photomicrographs obtained from longitudinal sections of the DMA are shown in Figures 29, 30, 31, and 32. Two photomicrographs are shown for each specimen representing regions that are in the highly stressed center region of the specimen and the less stressed region near the grip end. The two regions are approximately 25 mm apart.

It was thought that perhaps the stress state induced by the DMA test itself during cooling would influence the hydride distribution that was observed at room temperature. This was in fact the case for the Zr-2 128 ppm hydrogen specimen which has a difference

50 μm ———

Figure 29. Post-DMA test microstructure of Zr 15 ppm hydrogen DMA specimen. This photomicrograph is representative of the microstructure of the specimen in the mid-specimen region where the stresses are high and in the lower stress regions near the specimen clamps.

(a) 100 μm —

(b) 100 μm —

Figure 30. Post-DMA test microstructure of Zr 126 ppm hydrogen DMA specimen. (a) Highly stressed mid-specimen region. (b) Low stress region near specimen clamps.

50 μm ———

Figure 31. Post-DMA test microstructure of Zr-2 20 ppm hydrogen DMA specimen. This photomicrograph is representative of the microstructure of the specimen in the mid-specimen region where the stresses are high and in the lower stress regions near the specimen clamps

(a) 100 μm —

(b) 100 μm —

Figure 32. Post-DMA test microstructure of Zr-2 128 ppm hydrogen DMA specimen. (a) Highly stressed mid-specimen region. (b) Low stress region near specimen clamps.

in hydride distribution in the two regions. In the high stress region the hydrides are aligned longitudinally in layers across the specimen thickness. However, in the low stress region the hydrides are much shorter and aligned in a more random manner. The two regions of the Zr-2 20 ppm hydrogen specimen and the Zr 15 and 126 ppm hydrogen specimens had similar hydride distributions in the two regions. It may be that higher magnification examinations, such as with transmission electron microscopy, would reveal preferred hydride orientation differences that were not observed in the optical photomicrographs.

4.4 Post-Test Hydrogen and Oxygen Analysis

The oxygen and hydrogen content of the DMA specimens was determined following completion of the DMA testing. These results summarized in Table 12 show that the hydrogen certainly did not outgas during the DMA testing and that the oxygen content of the specimens may have increased by less than 200 ppm compared to the pre-test values. Because the specimens already had significant levels of oxygen in them, the increased oxygen levels are not expected to change any internal friction mechanisms, only perhaps increasing the relative peak height.

Table 12. Post-DMA test oxygen and hydrogen content of Zr and Zr-2 specimens.

Specimen	Hydrogen (ppm)	Oxygen (ppm)
Zr low hydrogen	21	320
Zr high hydrogen	130	420
Zr-2 low hydrogen	23	1230
Zr-2 high hydrogen	140	1360

5. Discussion

5.1 Internal Friction and Modulus Changes as Indicators of Hydride Precipitation

5.1.1 Continuous Cooling

For DMA to be an effective indicator of hydride precipitation during cooling it should exhibit at least two types of behavior consistent with the observations of Ritchie^(7,8) et al and Owen⁽⁹⁾ et al:

1. There must be some marked or un-ambiguous change in internal friction or modulus during cooling in the temperature range in which hydrides precipitate.
2. The precipitation indicator must be absent in very low hydrogen specimens, or move to lower temperatures consistent with the low hydrogen content.

Using Kearns et al's⁽²⁾ best fit data for Zr and Zr-2, the equilibrium hydrogen solvus for 126-128 ppm hydrogen is about 330-335°C. But hydrides don't nucleate at the equilibrium hydride solvus during the relatively fast cooling rates used in this investigation. Undercooling effects related to nucleation and growth phenomena depress the temperature at which hydrides nucleate. If the undercooling required to nucleate hydrides during cooling at 5°C/minute is 80°C, then precipitation could be lowered to about 250°C. Thus a marked change in internal friction or modulus should occur within the temperature range of approximately 250-335°C if DMA is sensitive to hydride precipitation.

Figures 33, 34, and 35 compare the DMA response of the 15 and 126 ppm Zr specimens at 3, 5, and 7 Hz, respectively. The scales of these graphs have been selected so as to magnify any variations that are present in the temperature range that hydrides are expected to occur in. Figures A33, A34, and A35 in Appendix 2 contain the full temperature range for these data. There are changes in modulus and internal friction at temperatures where hydride precipitation is expected. However, at all three frequencies these changes are always accompanied by a similar change in the respective low hydrogen specimen and therefore do not necessarily indicate hydride precipitation or for that matter, hydride related internal friction events. Also, the modulus below 250 °C of the 15 ppm hydrogen specimen is greater than that of the 126 ppm hydrogen specimen.

Figure 33. Effect of hydrogen on internal friction and storage modulus of Zr at 3 Hz.

Figure 34. Effect of hydrogen on internal friction and storage modulus of Zr at 5 Hz.

Figure 35. Effect of hydrogen on internal friction and storage modulus of Zr at 7 Hz.

This is contrary to what is expected because hydride precipitation should increase the modulus in accordance with Figures 10 and 11.

Figures 36, 37, and 38 compare the DMA response of the 20 and 128 ppm hydrogen Zr-2 at 3, 5, and 7 Hz, respectively. Figures A36, A37, and A38 in Appendix 2 contain the full temperature range for these data. Again, as with the Zr specimens, there are internal friction events and modulus inflections that are occurring within the temperature range in which hydride precipitation is expected. The features of the internal friction spectrum and the modulus inflections that are dissimilar in the hydrided and un-hydrided specimens that could potentially correlate to hydride precipitation are (1) the internal friction peaks at 5 and 7 Hz and (2) the modulus inflections occurring between 250 and 300°C.

Consider the internal friction peaks at 5 and 7 Hz. The onset temperature of these peaks shifts about 50°C. Furthermore, the 7 Hz peak has a high temperature tail that starts about 375°C, above the hydride solvus. This internal friction process is therefore not related to hydride precipitation. In as much as these peaks (and also the 3 Hz peak occurring at higher temperature) are present in the hydrided specimen but not the un-hydrided specimen, it is an apparent result that hydrogen is associated with specific internal friction processes.

Consider the modulus inflections between 250 and 300°C that occur in both the 20 and 128 ppm hydrogen Zr-2 specimens. Below 400°C the modulus of the 128 ppm

Figure 36. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 3 Hz.

Figure 37. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 5 Hz.

Figure 38. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 7 Hz.

hydrogen specimen is always greater than or about the same as the 20 ppm hydrogen specimen but the modulus of the 128 ppm hydrogen specimen increases more rapidly during cooling, particularly after the modulus inflection. The fact that the modulus of the 128 ppm hydrogen specimen increases more rapidly during cooling after the inflection may be indicative of some hydride precipitation related phenomenon, which is expected based on Figures 10 and 11. Irregardless of whether this modulus difference between the two specimens is related to some aspect of hydride precipitation in the Zr-2 128 ppm hydrogen specimen, it does not unambiguously define the temperature at which hydride precipitation occurs.

Although it was anticipated that some change in internal friction or modulus would unambiguously indicate hydride precipitation during cooling, this did not occur. The question remains as to why.

Ritchie et al⁽⁸⁾ suggests that the precipitation peak in pure Zr is associated with the formation of fresh dislocations around the hydride when precipitation occurs. The bowing of these dislocations under the oscillating stress field creates internal friction. The absence of the internal friction peak in Zr-2.5Nb in the same study was therefore related to the absence of these dislocations in that material. Irregardless of the exact mechanism of the precipitation peak, there is a microstructural difference between Zr alloys that dictates whether or not the precipitation peak is present. In the current

investigation it is rationalized that this microstructural feature is absent in the Zr and the Zr-2 alike and thus there is no internal friction precipitation peak.

The absence in the current investigation of modulus inflections of the type that are shown in Figures 10 and 11 that are correlated to hydride precipitation also needs to be considered. Although a possible hydride effect on the modulus of the Zr-2 128 ppm hydrogen specimen has been identified, this effect does not occur at a well defined temperature. Consider, for example, the data of Ritchie, et al⁽⁸⁾. Even though the internal friction precipitation peak is absent in Zr-2.5Nb, there is still a well defined, sharp inflection in the modulus. A possible explanation for the differences in the modulus inflections that accompany hydride precipitation as described by Ritchie et al and those observed in this investigation is in the nature of the test apparatuses that were used. Ritchie et al measured the modulus in pure shear and under resonant conditions. That is, the torsion apparatus was set into oscillation and allowed to vibrate at its natural frequency. The square of this natural frequency, f^2 , is proportional to the modulus. In the current investigation, the specimen is forced to vibrate at a fixed frequency in a complex stress state characteristic of the Model 983 DMA. Although the resonant frequencies that developed in Ritchie et al's experiments are comparable to those of the current investigation, the specimen is able to respond "naturally" in a resonant condition and is thus perhaps more sensitive to the microstructural changes accompanying hydride precipitation than is the fixed frequency method. Therefore, more DMA testing is

required to determine if operating the DMA in the natural frequency vibration mode will develop well-defined modulus inflections that are unambiguously correlated to hydride precipitation.

5.1.2 Isothermal Hold

The isothermal hold data do not show any outright signs directly correlated to hydride precipitation. The qualitative nature of the isothermal hold DMA data were very similar at all of the hold temperatures, even for the 375°C specimen for which hydride precipitation is not possible. It is interesting to compare the 300 and 325°C conditions for which hydrides should exist and the 350 and 375°C conditions for which hydrides should not exist. The internal friction of the 300 and 325°C specimens decayed to zero whereas the 350 and 375 °C specimens maintained a high background internal friction level. This may be indicating a relative effect as to whether or not hydrides are present or not. For example, the high hydrogen content within the matrix for temperatures above the hydride solvus may explain the higher background internal friction compared to temperatures below the hydride solvus where there is a smaller amount of hydrogen in solution. This effect is interesting and could be explored further to determine a potential correlation between the amount of hydrogen in solution and the level of internal friction.

The major changes in the modulus and internal friction during the isothermal experiments occurred during the transient to thermal equilibration. It is possible that the hydride transformation occurs rapidly, in the time frame of the cool down. Hydride

transformation during cooling is thought to be very rapid, occurring within seconds⁽¹⁾. If the transformation occurred rapidly then it would not be observed in the current results because of the slow thermal equilibration lag.

5.2 Identification of Internal friction Peaks

The observed internal friction peaks cannot be directly associated with hydrogen precipitation. It remains to attempt to identify their origin. The context of this discussion will center on what other investigators have found in similar investigations.

Asundi et al⁽¹¹⁾ have investigated the internal friction of Zr-oxygen-metal alloys between 300 and 750°C and at 1.3 Hz. They found that pure zirconium containing only oxygen as an impurity does not develop an internal friction peak. A grain boundary phenomenon occurring above 500°C was identified by comparing specimens with various grain sizes. Two oxygen interaction peaks developed when there was a substitutional alloying addition such as iron; some of these peaks occurred between 350 and 450°C. The activation energies for the oxygen interaction peaks ranged from 167-351 kJ/g-mol.

Ritchie⁽¹²⁾ et al have determined the internal friction spectrum of single crystal Zr containing 5000 ppm oxygen between ambient and 700°C. Internal friction peaks that developed in the vicinity of 450°C and 3 Hz were observed and used to calculate an activation energy of 192 kJ/mol. The peak was attributed to the presence of oxygen by

comparison to a specimen containing only 120 ppm oxygen that did not show a similar peak.

Povolo et al⁽¹³⁾ have investigated the high temperature internal friction (HTIF) of polycrystalline Zr-4. Two internal friction maxima were observed. A peak at 1.82 Hz and 634°C was attributed to sliding of particle-free grain boundaries. A peak at 1.68 Hz and 710°C was attributed to the sliding of boundaries blocked by small precipitates.

Ritchie et al⁽¹⁴⁾ have observed a large peak at 420°C and 2.5 Hz in the internal friction spectrum of pure polycrystalline zirconium containing 27 ppm hydrogen and 120 ppm oxygen. This peak was dependent on thermal cycling and was attributed to thermally assisted un-pinning and movement of dislocations produced by hydride nucleation.

One way of identifying internal friction peaks is by similitude of activation energies. By similitude, if the activation energy of a given internal friction process is similar to that of a known process, such as diffusion of some element, then it may be that the two processes are identical. The simplest processes to understand in terms of an internal friction mechanism would be atomic diffusion. The activation energies for diffusion of oxygen⁽¹⁵⁾ and hydrogen⁽¹⁾ are 44 and 35 kJ/mol, respectively. These activation energies do not correlate with any of the activation energies that were observed in this study (15, 18, 19, and 29 kJ/mol). Thus, the internal friction peaks that have been observed are not due to bulk diffusion of oxygen or hydrogen. The possibility exists that the observed

relaxation processes correlate with grain boundary diffusion or pipe diffusion along dislocations. The activation energies for these types of processes are typically 1/3 to 1/2 that of bulk diffusion. Thus grain boundary or pipe diffusion of interstitial elements such as hydrogen or oxygen is consistent with the internal friction processes that were described in the results section.

It is evident that the specific internal friction processes that have been observed in this investigation are still not conclusively attributed to any one particular mechanism. The internal friction peaks observed in the current investigation have been shown not to be unambiguously caused by hydride precipitation or simple bulk diffusion of oxygen or hydrogen. The peaks may be caused by grain boundary or pipe diffusion of interstitial elements such as oxygen or hydrogen. The peaks are unlikely to be due to grain boundary sliding which generally occurs above the temperature range ($\sim 0.4 T_m$) of the current investigation. The peaks existing in Zr-2 above the temperature at which hydrides are dissolved may be due to interactions with oxygen or bowing of dislocations produced from the hydrides present at lower temperatures; the high temperature peaks shown to be associated with hydrogen in the Zr-2 specimen may be an interaction of hydrogen with oxygen or with dislocations. But it is unclear why a similar peak is not observed in hydrided Zr. The peaks that are reported to occur below the temperature at which hydrides are precipitated have not been reported in the literature and are of an unknown origin.

5.3 Modulus Anomalies

The elastic modulus of Zr and Zr-2, determined by a variety of dynamic and static techniques^(10,16-19), is shown in Figure 39. These data provide a comparison to the current modulus data. The elastic modulus of Zr and Zr-2 varies from approximately 90 GPa at room temperature and drops to approximately 80 GPa at 500°C. The modulus data falls within a relatively narrow band and this implies that alloying elements have only a small effect on the elastic modulus of Zr and Zr-2.

The Zr and Zr-2 modulus data obtained by DMA at 5 Hz is included in Figure 39 for comparison. It is obvious that there is a considerable discrepancy between the current results and those of other investigators. The anomaly is caused by the internal friction processes that are present at the temperatures and frequencies investigated. It is interesting to note that at lower temperatures, where the internal friction has been found to be low, the modulus data is consistent with other investigators. This point shows the importance of eliminating internal friction processes when making modulus measurements.

6. Conclusions

Dynamic mechanical analysis of hydrided and unhydrided zirconium and Zircaloy-2 has shown the existence of internal friction events that are indicative of movements on an atomic scale. The activation energies for these internal friction processes are between 15

Figure 39. Comparison of DMA storage moduli to dynamic modulus of Zr and Zr-2 to published values.

and 29 kJ/mol. A comparison of the hydrided and unhydrided materials indicates that hydrogen influences the internal friction spectra. However, Zr and Zr-2 do not exhibit an internal friction hydrogen precipitation peak during cooling as has been described by other investigators for pure Zr and V.

The storage moduli measured in the dynamic mechanical analysis of hydrided and unhydrided zirconium and Zircaloy-2 have anomalously large temperature dependencies compared to published values. This anomalous behavior is correlated with the existence of internal friction events at the temperatures and frequencies that were investigated. Inflections in the modulus could not be correlated to hydride precipitation in the hydrided Zr. Inflections in the hydrided Zircaloy-2 material may be associated with hydride precipitation. However, these inflections could not be correlated conclusively with the onset of hydride precipitation. Post-test photomicrographs showed that zirconium hydrides can have preferred orientations with respect to the stress field that they are grown in. This may lead to variations in modulus when hydrides are present and may have some effect on the modulus inflections that were observed.

The current experimental program failed to answer the original question that was posed, i.e., is there a difference in the temperature at which zirconium hydrides nucleate during cooling in Zr and Zr-2. This information is necessary to model the mechanism of the preferentially hydrided liner. Specifically, the DMA technique was not able to correlate internal friction peaks or modulus inflections with hydride precipitation during

cooling. It has been proposed that the reason for this is (1) related to the Zr and Zr-2 materials used, and (2) related to the DMA technique itself.

7. Recommended Future Work

The most promising area of future work is to evaluate whether or not a resonant frequency method (compared to the fixed frequency method used in this study) is able to detect hydride precipitation in Zr and Zr-2. Once a hydride precipitation indicator is observed then the method can be extended to investigating the Zr and Zr-2 hydrogen system under varying cooling rates and hydrogen contents.

An additional area of work that might be useful in understanding hydride precipitation phenomena is related to stress-biased experiments. If a precipitation indicator was identified for some set of experimental conditions, then biasing the specimen so that it has a mean tensile or compressive stress will elucidate the role of stress on nucleating hydrides.

8. References

1. Northwood, D.O., and Kosasih, U., "Hydrides and Delayed Hydrogen Cracking in Zirconium and its Alloys," *International Metals Reviews*, Vol. 28, No. 2, 1983, pp. 92-121.
2. Kearns, J.J., "Terminal Solubility and Partitioning of Hydrogen in the Alpha Phase of Zirconium, Zircaloy-2, and Zircaloy-4," *Journal of Nuclear Materials*, Volume 22, 1967, pp. 292-303.
3. Slattery, G.F., "The Terminal Solubility of Hydrogen in Zirconium Alloys Between 30 and 400°C," *Journal of the Institute of Metals*, vol. 95, 1967, pp. 292-303.
4. Erickson, W.H., and Hardie, D., "The Influence of Alloying Elements on the Terminal Solubility of Hydrogen in alpha Zirconium," *Journal of Nuclear Materials*, Volume 13, No. 2, 1964, pp. 254-262.
5. Ritchie, I.G., and Sprungmann, K.W., "Hydride Precipitation in Zirconium Studied by Low-Frequency Pendulum Techniques," *Colloque de Physique*, Vol. Colloque C9 V44, No. 12, 1983, pp. 313-318.
6. Ritchie, I.G., and Pan, Z.L., "Internal Friction and Young's Modulus Measurements in Zr-2.5Nb Alloy Doped with Hydrogen," *M³D: Mechanics and Mechanisms of Materials Damping*, ASTM STP 1169, V.K. Kinra and A.

- Wolfenden, Eds., American Society for Testing and Materials, Philadelphia, 1992, pp. 385-395.
7. Owen, C.V., and Scott, T.E., "Relation Between Hydrogen Embrittlement and the Formation of Hydride in the Group V Transition Metals," *Metallurgical Transactions*, Vol. 3, July 1972, pp. 1715-1726.
 8. Dieter, G.E., Mechanical Metallurgy, McGraw-Hill, New York, 1961.
 9. Dowling, N.E., Mechanical Behavior of Materials, Prentice Hall, New Jersey, 1993.
 10. Armstrong, P.E., Brown, H.L., "Dynamic Young's Modulus Measurements above 1000°C on Some Pure Polycrystalline Metals and Commercial Graphites," *Transactions of the Metallurgical Society of AIME*, 962, Volume 230, Aug. 1964.
 11. Asundi, S., Mishra, M.K., "Internal Friction Studies in Dilute Zirconium Alloys," *Canadian Metallurgical Quarterly*, Vol. 11, No. 1, 1972, pp. 69-77.
 12. Ritchie, I.G., Rosinger, H.E., Atrens, A., "Anelastic Internal Friction and the Diffusion of Oxygen in Alpha-Zirconium," *Journal of Nuclear Materials*, Vol. 62, 1976, pp. 1-8.
 13. Povolo, F., Molinas, B.J., "High-Temperature Internal Friction in Polycrystalline Zircaloy-4," *Journal of Materials Science*, Vol. 21, 1986, 3539-3547.
 14. Ritchie, I.G., Atrens, A. Blair, D.G., "Anomalously Large Amplitude Dependent Damping and Modulus Defect in Polycrystalline Zirconium," *ICIFUAS-6*

- Proceedings of the 6th International Conference on Internal Friction and Ultrasonic Attenuation in Solids, July 1977, Tokyo, Japan, pp. 639-643.
15. Ritchie, I.G., Atrens, A., "The Diffusion of Oxygen in Alpha-Zirconium," Journal of Nuclear Materials, 67, 1977, pp. 254-264.
 16. Miller, G.L., Metallurgy of the Rarer Metals - Zirconium, Academic Press Inc., London, 1957.
 17. Northwood, D.O., London, I.M., and Bahen, L.E., "Elastic Constants of Zirconium Alloys," Journal of Nuclear Materials, Vol. 55, 1975, pp. 299-310.
 18. Douglass, D.L., The Metallurgy of Zirconium, Atomic Energy Review, Supplement 1971, IAEA.
 19. Scott, D.B., "Physical and Mechanical Properties of Zircaloy 2 and 4," Westinghouse Electric Corporation, Atomic Power Division, Report No. WCAP-3269-41, May 1965.

Appendix 1

Detailed DMA Equations

The following set of equations, obtained directly from the TA Instruments Model 983 DMA operators manual, are used to calculate the moduli by combining the results of equations that describe the physical DMA instrument with parameters derived from viscoelastic beam bending theory. These equation were derived to account for the contribution of instrument calibration constants to specimen modulus. The instrument correction is subtracted from the raw modulus, and the result is multiplied by the specimen geometry constants to yield the corrected modulus.

(1) Shear storage modulus

$$G' = (2Jk^2 - 2K') \frac{\beta^2 + \gamma^2}{\beta} \frac{L'}{\beta} - \frac{\gamma}{\beta} G''$$

(2) Shear loss modulus

$$G'' = [2J(wd)] - 2K'' \frac{\beta^2 + \gamma^2}{\beta} \frac{L'}{\beta^2 A} + \frac{\gamma}{\beta} G'$$

(3) Flexural storage modulus

$$E' = 2(1 + \nu)G'$$

(4) Flexural loss modulus

$$E'' = 2(1 + \nu)G''$$

(5) Tan delta

$$\tan(\delta) = \frac{G''}{G'} \text{ or } \frac{E''}{E'}$$

where:

$$\beta = \alpha + \frac{L'^2 A}{24(1 + \nu)I} + \frac{A}{L'}(Jc' G' + Jc'' G'')$$

$$\gamma = \left(\frac{A}{L'}\right)(Jc' G'' - Jc'' G')$$

$$k^2 = \frac{Mo}{2J\theta_0} \cos(\delta) + \omega^2$$

$$(wd) = \frac{Mo}{2J\theta_0} \sin(\delta)$$

$$\omega = 2\pi f$$

$$Mo = \frac{2J}{R} 4\pi f^2$$

$$\theta_0 = \frac{a}{R}$$

L' = effective sample length (mm)

= measured $L + \Delta L$

B = distance between pivot centers (mm)

= sample length + $2D$

$A = \text{cross – sectional area of sample} (mm^2)$

$I = \text{geometric inertial moment of cross – section} (mm^4)$

$$= \frac{T^3 W}{12}$$

Measured Signals

$V = \text{drive signal (mV)}$

$f = \text{frequency (Hz)}$

$\delta = \text{phase angle (radians)}$

Experimental Parameters

$T = \text{thickness of rectangular specimen (mm)}$

$W = \text{width of rectangular specimen (mm)}$

$L = \text{length of specimen (mm)}$

$a = \text{oscillation amplitude (0.5 mm)}$

Specimen Constants

$\Delta L = \text{length correction constant (= 2.0 mm)}$

$\nu = \text{Poisson's ratio}$

$\alpha = \text{shear distortion factor (1.5)}$

Instrument Constants

D = clamping distance (8 mm)

R = distance from flexure pivot center to point at which "a" is measured in instrument calibration (127.85 mm)

J = single arm inertial moment (kg m²)

C' = drive signal constant (mm/mV sec²)

K' = instrument parallel storage stiffness (N m)

K'' = instrument parallel loss stiffness (N m)

Jc' = instrument series storage compliance (μm/N)

Jc'' = instrument series loss compliance (μm/N)

$$= \frac{Jc_m'' \sqrt{k^2 / 4\pi^2}}{f_m}$$

f_m = frequency at which Jc_m'' was measured (Hz)

These calculations are complicated by the fact that the instrument correction terms β and γ are dependent on G' and G''. They are solved by an iterative process that stops when the change in modulus after an iteration is less than one percent.

Flexure Stress (MPa)

$$\sigma = \frac{24\pi^2 JCVL}{BRTW}$$

Shear Stress (MPa)

$$\sigma = \frac{8\pi^2 JCV}{BRTW}$$

Flexure Strain (%)

$$\varepsilon = \frac{3TaB}{L^2 R} 100$$

Shear Strain (%)

$$\varepsilon = \frac{aB}{LR} 100$$

Appendix 2

Additional Internal Friction and Storage Moduli

Comparative Data for Zr and Zr-2

Figure A33. Effect of hydrogen on internal friction and storage modulus of Zr at 3 Hz.

Figure A34. Effect of hydrogen on internal friction and storage modulus of Zr at 5 Hz.

Figure A35. Effect of hydrogen on internal friction and storage modulus of Zr at 7 Hz.

Figure A36. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 3 Hz.

Figure A37.. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 5 Hz.

Figure A38. Effect of hydrogen on internal friction and storage modulus of Zr-2 at 7 Hz.