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Internal Friction Peaks Associated with Hydrides in Zr and Zr-2.5Nb

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Abstract. Internal friction peaks P_1 , P_2 and P_3 were determined by the composite oscillator technique (APUCOT) at 40 and 120 kHz in unalloyed Zr + H and in Zr-2.5Nb + H. The effect on the peaks of hydrogen content, thermal cycling and ageing was investigated. P_1 can be increased by misfit dislocations due to hydrides. The height of P_2 is proportional to the total content of hydrogen while P_3 depends on the hydride morphology.

1. INTRODUCTION

A gradual pickup of hydrogen and its isotopes during service can occur in Zr-2.5Nb, an alloy used for pressure tubes of CANDU® nuclear reactors, as well as in other Zr alloys used in the core of nuclear reactors. When the hydrogen content in these alloys exceeds the terminal solid solubility (TSS), the components could be susceptible to a sub-critical crack growth process called delayed hydride cracking (DHC) [1]. Knowledge of both the TSS [2, 3] and the morphology and types of the hydrides are important in understanding DHC. The internal friction (IF) technique has been shown to be a powerful tool for studying hydrogen in metals. The spectrum of IF peaks associated with hydrogen in unalloyed Zr (hereinafter referred to as 'Zr') and Zr alloys has been extensively investigated. In the high temperature range, a truncated peak [4] situated at the TSS temperature is a typical phase-transformation peak accompanied by a knee-point in the corresponding elastic modulus curve. In the low temperature range, three relaxation peaks [5], P_1 , P_2 and P_3 , are associated, respectively, with dislocations and hydrides. In Zr, peaks P_1 , P_2 and P_3 were investigated in [6-11]. Some of the results agreed with each other, but some were in disagreement [10] and the activation energies of P_2 and P_3 were scattered [11]. Different mechanisms responsible for these peaks were proposed. The present work extends previous studies on the Zr-H system to the technologically important Zr-2.5Nb pressure tube material containing low levels of hydrogen. It describes new experimental observations concerning the aforementioned peaks.

2. EXPERIMENTAL DETAILS

Mainly two kinds of material were used: specimens made from reactor-grade Zr plate and from sections of Zr-2.5Nb pressure tubes. The specimens of Zr-2.5Nb were cut with their long axis either along the tube's transverse or axial direction. The microstructure of the autoclaved tubes consists of elongated α -phase grains with hcp surrounded by a continuous, intergranular β phase with bcc. Dimensions of all specimens are 3 mm by 3 mm by 46 mm. The Zr specimens were doped with hydrogen by a gaseous technique at about 500°C and homogenized for 10 days at 400°C. Using a Ni coating technique [3], the Zr-2.5Nb specimens were gaseously charged with hydrogen at 250°C, which helped preserve the original α/β microstructure of the material. Simultaneous measurements of IF and Young's modulus were carried out using the Automatic Piezoelectric Ultrasonic Composite Oscillator Technique (APUCOT), details of which have been given elsewhere [12].

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3. RESULTS AND DISCUSSION

3.1 Peak P_1

If peak P_1 has been observed in deformed Zr [8-11] and Zr-2.5Nb [5]. The relaxation strength (height of peak) increases with level of tensile deformation. In H-doped Zr specimens, the dependence of the peak height on hydrogen content is linear in the range of $C_H < 6$ at.% [11]. The activation energy of 0.22 ± 0.02 eV, determined by the peak's temperature shift with frequency, is in the range from 0.20 to 0.32 eV previously reported. The relationship between peaks P_1 and P_2 (Fig. 1) is interesting. In a Zr-2.5Nb + 1.4 at.% H specimen annealed at 400°C, a small P_1 peak appeared during first cooling and warming. The peak increased in height after rewarming through the P_2 peak and cooling from 170°C. In subsequent tests, an enhanced P_1 peak was reproduced. The solubility of hydrogen at 170°C may reach about 0.2 at.%, which is 1/7 of the total H content. During subsequent cooling, hydrogen atoms in solid solution can migrate back to the existing, undissolved hydrides and coarsen them. Likely, fresh misfit dislocations were punched out, as demonstrated in [13]. On the other hand, most of the original dislocations were probably pinned during the initial hydrogen charging and annealing, but in the warming up phase to 170°C, some of the defects responsible for the pinning may have migrated away, depinning some dislocations. The increase of P_1 could be attributed to both the depinning of the existing dislocations and the creation - due to hydride growth - of fresh, unpinned misfit dislocations.

Figure 1: The effect of thermal cycles on P_1 and P_2 .

Figure 2: Dependence of P_2 on hydrogen content in Zr.

3.2 Peaks P_2 and $P_2\gamma$

A typical, thermally activated relaxation peak P_2 at 80°C was observed with the APUCOT at 40 kHz in Zr and Zr-2.5Nb containing hydrogen from 0.5 to 55 at.%, as well as in Zr-3.5Sn-Mo-Nb (Excel) [3]. The height of P_2 is proportional to the total content of hydrogen (Figs. 2 and 3). The activation energy of 0.56 ± 0.04 eV and $\tau_0 = 2 \times 10^{-13}$ s obtained in the present work falls in the range of 0.52 to 0.67 eV given in [6-11]. No significant effect of thermal cycle, ageing and sample orientation on the P_2 peak height was observed. The width of P_2 was analyzed using the method used in [14] with the theoretical peak function given by Nowick and Berry [15]. A good fit between measured data, such as curve 6 of Fig. 3 and curve 1 of Fig. 6, is obtained with the peak function parameter, $\beta = 1$, which is wider than the standard single-relaxation-time peak with $\beta = 0$; the low temperature side is even wider than for a curve with $\beta = 1$ due to the contribution from a small peak, which we denote $P_2\gamma$. Two peaks P_2 and $P_2\gamma$ were found in two specimens of Zr-3.5Sn-Mo-Nb + 1.2 at% H, respectively, as shown in Fig. 4. In a sample fast cooled from 400°C, a peak $P_2\gamma$ at 48°C and a peak P' at 150°C were, separately, determined, but in another annealed sample, only the P_2 peak at 80°C was obtained. On curve 3 of Fig. 4, both a large P_2 at 80°C and a trace of $P_2\gamma$ at 48°C were both observed in a rapidly cooled Zr-2.5Nb +

1.6 at.% H sample, but $P_2\gamma$ disappeared in the subsequent thermal cycle. According to electron microscope observations [16], γ hydrides are precipitated at high cooling rates whereas slow cooling rates lead mainly to δ hydrides. This suggests that the stable P_2 peak is mainly associated with the equilibrium δ hydrides, but its wider tail at low temperatures may be associated with the residual presence of γ hydrides, while the faint $P_2\gamma$ peak should also be associated with the presence of metastable γ hydrides. Both peaks P_2 and $P_2\gamma$ may be due to the stress-induced rearrangement of hydrogen atoms or pairs inside either δ hydrides (fcc lattice) or γ hydrides (fct lattice). This is similar to the Zener relaxation in fcc metals. The relative proportion of, and the transition between, γ and δ hydrides depends on factors such as the microstructure, the extent and number of thermal cycles, ageing, hydrogen content, etc. This might explain the large scatter in the reported values of the activation energy of P_2 , and why the $P_2\gamma$ peak is not always present. It can also be seen from Fig. 3 that the background IF increases with hydrogen content as the concentration in solution increases. The IF also reaches a saturation value when the hydrogen concentration in solution reaches its limiting value defined by the TSS at that temperature. These phenomena are very repeatable, such as shown in Fig. 4 of [3]. At present, it is not clear what mechanism contributes to the background IF.

Figure 3: Dependence of P_2 height on total H content.

Figure 4: P_2 and $P_2\gamma$ formed in Excel and Zr-2.5Nb.

3.3 Peaks P_3 and P'

Two peaks P' and P_3 were, respectively, observed in the range of 150 to 180°C in different samples. The temperature of the sharp P' peak was not shifted with frequency, but its height was significantly reduced, even vanishing, when increasing the frequency to 120 kHz. However, both the height and temperature of P' increased with increase in maximum temperature of the thermal cycle and with ageing (Fig. 5). The P' peak is likely a phase-transformation peak. Others have shown that a reduction in the proportion of metastable γ hydrides in favour of the equilibrium δ hydrides occurs in the temperature range from 150 to 250°C [16]. The P' peak may be a manifestation of the transition between these two kinds of hydrides. The peak denoted P' in [11] is likely the same P' peak observed in the present work. Other authors [6-9] have not reported this peak because their tests were carried out in the temperature region below 150°C. A thermally activated relaxation peak P_3 at 180°C was observed in a specimen of Zr-2.5Nb + 1.6 at.% H quenched from 400°C (Fig. 6). The activation energy of 0.74 ± 0.04 eV and $\tau_0 = 6 \times 10^{-14}$ s determined in this work is close to the range of 0.72 to 0.87 eV reported in [6-11]. After thermal cycling to different maximum temperatures up to 430°C, which is higher than the TSS temperature for this sample, the P_3 peak progressively disappeared. The sample was quenched again from 400°C, and similar curves as in Fig. 6 were, reproducibly, obtained. The P_3 peak may be due to the stress-induced growth and shrinkage of hydrides caused by the migration of hydrogen atoms through their interfaces, as in [5]. Its presence may be associated with aspects of the morphology and orientation of the hydrides in the specimen. Thus the appearance of the P_3 peak was

favoured in quenched or annealed specimens cut with their long axes oriented along the transverse direction of the pressure tube. In axially oriented specimens the P_3 peak was not observed in annealed specimens, even when the latter contained large amounts of δ hydrides, e.g., Fig. 2. The fact that this peak is observed in quenched samples, for which γ hydrides are expected, means that it cannot simply be identified with the presence of δ hydrides, as suggested in [8]. In transverse samples, because of the texture of the material, the hydride platelets making up the internal structure of the hydrides that are visible under optical magnification have an edge normal parallel to the displacement of the induced longitudinal vibration. Since growth and shrinkage of a hydride platelet is likely only possible at its edges, this orientation is optimal for induced phase transfer across the interface. Quenching may produce shorter clusters of hydrides with fresh edges that are more capable of responding to the induced vibrations. No peak is found in annealed axial specimens, since in this orientation the normal to one of the hydride platelet edges is at an angle to the direction of induced vibration; however, quenching may help this less favourable orientation.

Figure 5: Increase of P' with $T_{\max}$ of thermal cycles.

Figure 6: Decrease of P_3 with $T_{\max}$ of thermal cycles.

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