

Part 1 ?

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HYDROGEN-INDUCED DELAYED CRACKING:

2. EFFECT OF STRESS ON NUCLEATION,  
GROWTH AND COARSENING OF ZIRCONIUM  
HYDRIDE PRECIPITATES

by

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ABSTRACT

There is strong motivation for understanding the factors controlling zirconium hydride reorientation under stress because of the important role this plays in hydrogen-induced crack growth and/or crack initiation in zirconium and its alloys, particularly under thermal cycling conditions. Following an approach developed by Sauthoff, an analysis of the orienting effect of external stress on the nucleation, growth and coarsening of  $\gamma$  and  $\delta$ -zirconium hydride precipitates in zirconium and its alloys is presented. The analysis is based on a previous theoretical study of some of the factors affecting hydride solubility in stressed and unstressed solids. Expressions are derived for the effect of stress on nucleation, growth and coarsening. We conclude, on the basis of these that the preferential orientation of hydride precipitates under stress is most efficient during the nucleation stage. The reason for this is that the overall driving force for nucleation, for the chosen parameters and the usual experimental conditions, is fairly small. Therefore, the driving force for orientating under stress can be a substantial fraction of the overall driving force. The analysis shows that hydride growth is unlikely to play a role in preferential orientation, but coarsening could be important under carefully chosen experimental conditions, which may be relevant to the hydride-cracking process.

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## 1. INTRODUCTION

There is strong motivation for understanding the factors controlling zirconium hydride reorientation under stress, because of the important role this plays in hydrogen-induced crack growth and/or crack initiation in zirconium and its alloys, particularly under thermal cycling conditions (for a recent review, see Puls et al. [1]). Previously, Ellis [2] studied this problem in an attempt to explain hydride reorientation in uniaxially stressed zirconium alloys cooled from a temperature at which hydrogen was mostly in solution. Considering only the nucleation and growth stages, he concluded that reorientation was governed mainly by stress-assisted preferential nucleation. In a later study, however, Ellis and Simpson [3] concluded that, under certain circumstances, growth could also be a governing factor in stress-assisted hydride reorientation. Recently, Sauthoff [4-6] presented a detailed theoretical and experimental analysis of the orienting effect of an external stress on the nucleation, growth and coarsening of tetragonally misfitting Au-rich plates in an Fe-Mo-Au alloy. For this system, Sauthoff demonstrated that under the chosen experimental conditions, coarsening was the rate-determining step.

In a previous report [7] and subsequent modifications [8,9], (hereinafter referred to as I) we presented a general theoretical analysis of some of the factors affecting hydride solubility in stressed and unstressed solids. In the following, we re-examine the problem, first considered by Ellis [2], of the factors influencing the orienting tendency of zirconium hydride precipitates, by making use of the results developed in I, combined with classical nucleation theory and the thermodynamics of growth and coarsening. We follow closely the methodology of Sauthoff, relevant to misfitting precipitates. Our objective is to determine which of the three stages, nucleation, growth or coarsening, is most effective in causing the stress-assisted orientation of hydrides, thereby allowing us to determine the conditions under which stress orientation can be achieved, or avoided.

The paper is organized as follows. In the next section we present the general relations developed to describe homogeneous and heterogeneous nucleation in solids, and derive specific relations relevant to zirconium hydrides in stressed and unstressed solids. Next, we make use of the solubility studies carried out in I to determine whether, in these cases, hydrides precipitated homogeneously or heterogeneously. The values of certain important parameters are determined on the basis of this analysis. These parameters are used in a subsequent section to evaluate the stress-reorienting potency of the nucleation stage. The following two sections apply the same considerations to the growth and coarsening stages, respectively. Finally, we consider the results in relation to hydride distributions in zirconium-based reactor pressure-tube material.

## 2. NUCLEATION

### 2.1 GENERAL

In this section we present some general relations derived to describe classical homogeneous and heterogeneous nucleation in solids [10]. The steady-state nucleation rate is given by

$$J = Z s_k C_k^0 \quad (1)$$

where  $J$  is the number of nuclei formed per unit volume and unit time,  $s_k$  is the rate at which atoms are added onto the critical nucleus, and  $Z$  is the Zeldovich factor. This latter factor is typically around 0.1 and accounts for the fact that some supercritical nuclei decompose and that, in addition, we do not actually have a metastable equilibrium concentration of critical nuclei, as given by  $C_k^0$ . The metastable equilibrium concentration  $C_k^0$  is given by

$$C_k^0 = \frac{N_0}{C_H} \exp(-\Delta G_k/kT) \quad (2)$$

we require an increase in the mean particle radius by a factor  $4^{1/3} = 1.6$ . Thus, an increase by 60% of the mean particle radius will result in com-

where  $\bar{C}_H$  is the atom fraction of solute (hydrogen) in the critical nucleus, and  $\Delta G_k$  is the free energy of formation of a critical nucleus. For homogeneous nucleation,  $N_0$  is the number of atom sites per unit volume, whereas for heterogeneous nucleation it is the number of heterogeneous nucleation sites per unit volume. Typically, the number of heterogeneous nucleation sites is many orders of magnitude less than the number of atom (homogeneous) sites.

Usually, the free energy of nucleus formation,  $\Delta G_k$ , is made up of three terms: the chemical free energy to form the nucleus from solid solution, the interfacial energy and the elastic strain and interaction energies. (Explicit expressions for  $\delta$ -hydride plates and  $\gamma$ -hydride needles are derived in Appendix A.) The difference between homogeneous and heterogeneous nucleation resides mainly in the relative contributions to the total free energy of the last two energies mentioned above. Thus, for heterogeneous nucleation on, for instance, grain boundaries, the interfacial energies will be greatly reduced. On the other hand, nucleation on dislocations generally reduces the contribution due to the elastic strain energy. A reduction in  $\Delta G$  usually increases  $J$  more than a reduction in nucleation sites decreases it, and thus, except for exceptionally large undercooling, heterogeneous nucleation is favoured in most polycrystalline solids.

The kinetic factor,  $s_k$ , depends on the shape of the critical nucleus and the type of nucleation. For the disc- and needle-shaped precipitates considered here, we have the following expressions (to simplify the expressions, we have assumed that discs are equivalent to plates) [10]:

1. needles (homogeneous nucleation)

$$s_k = 4\pi \bar{C}_H^2 \cdot N_0 \cdot \frac{D_H}{d} \quad (3)$$

as the sample would have to be held at just below the nucleation tempera-

2) discs (homogeneous nucleation)

$$t_k = 2\pi a_k^2 \cdot \bar{C}_H \cdot N_0 \cdot \frac{D_H}{d} \quad (4)$$

3) discs on a grain boundary (heterogeneous nucleation)

$$t_k = 2\pi a_k \cdot \bar{C}_H \cdot N_0 \cdot D_H^{gb} \quad (5)$$

where  $c_k$  and  $a_k$  are the critical dimensions of the nucleus defined in Appendix A,  $\bar{C}_H$  is the concentration of hydrogen in the supersaturated solution,  $D_H$  and  $D_H^{gb}$  are, respectively, the diffusion coefficients of hydrogen in the bulk and in the grain boundaries of the zirconium matrix, and  $d$  is the jump distance for H in the Zr lattice. In Equation (5)  $N_0$  takes the value for homogeneous nucleation.

As derived in Appendix A, the critical nucleation energy for  $\delta$ -hydride plates is given by

$$\Delta G_k = \frac{2}{3} \pi \frac{\bar{\gamma}_p^3}{[c(\Delta g_{chem} - A_1 - cA_2 - \Delta g_{int})]^2} \quad (6)$$

and for  $\gamma$ -hydride needles by

$$\Delta G_k = \frac{16\pi}{3} \frac{\bar{\gamma}_n^3}{c(\Delta g_{chem} - \Delta g_{strain} - \Delta g_{int})^2} \quad (7)$$

with  $c = c_k/a_k$  being the ratio of the critical dimensions determined from Equations (A.19-A.20) and (A.27-A.28), respectively, while  $\Delta g_{chem}$ ,  $A_1 - cA_2$ ,  $\Delta g_{strain}$ ,  $\Delta g_{int}$ ,  $\bar{\gamma}_p$  and  $\bar{\gamma}_n$  are defined in Appendix A. It is evident that  $\Delta G_k$  is a sensitive function of both  $\bar{\gamma}$ , the effective surface energy of the nucleus and, to a lesser extent, the difference between the chemical driving force and the strain and interaction energy terms.

## 2.2 EFFECTS OF EXTERNAL STRESS

The above results include the contributions due to both accommodation (internal) and applied (external) stress on hydride nucleation. When the external stress effects are small compared to the other terms, it is possible to derive an approximate relation that shows the effect of external stress on hydride nucleation more clearly, as follows.

The interaction energy per unit volume of a hydride under an external stress is given generally by (7-8)

$$\Delta g_{int} = \left( -\sigma_{ij}^A \right) \left( e_{ij}^T \right) \quad (8)$$

where  $\sigma_{ij}^A$  are the applied stresses (positive when tensile) and  $e_{ij}^T$  the transformation or stress-free misfit strains of the hydride, as defined in I. In Equation (8), summation over repeated indices is implied, with the indices  $i, j$  ranging from 1 to 3. Generally, we are interested in situations where the stresses in one direction are larger than those in the others, such as when applying a uniaxial tensile stress. In this case, for instance, the  $\delta$ -hydrides, because their misfits are anisotropic, will have a greater negative interaction energy if they line up with their plate normals parallel to the direction of the applied stress. We call hydrides that do this "aligned", and those that do not, and are at  $90^\circ$  to this direction, "non-aligned". Assume for simplicity that hydrides in a polycrystalline solid, because of texture effects, can only be found in these two directions. We now wish to determine the difference in nucleation frequency between "aligned" and "non-aligned" hydrides.

It will be convenient to define a quantity  $B$  given by

$$\Delta g_{int} = -B \quad (9)$$

which is positive when both stresses and misfits are positive, as is the case for zirconium hydrides under tensile loadings. Separating out the contribution due to the external stress in  $\Delta g_{\text{chem}}$  by writing

$$\Delta g_{\text{chem}} = \Delta g'_{\text{chem}} - (\pi/\bar{V}_{\text{hyd}}) p \bar{V}_{\text{H}}$$

where  $\Delta g'_{\text{chem}}$  is the chemical driving force at zero stress, and the remaining symbols are as defined in Appendix A, we can express the critical nucleation energy (using Equation (A.22)) by

$$\Delta G_k = \frac{2}{3} \pi \frac{\bar{V}_p^3}{\{c[\Delta g'_{\text{chem}} - A_1 - cA_2 + B - (\pi/\bar{V}_{\text{hyd}}) p \bar{V}_{\text{H}}]\}^2}$$

When  $|B - (\pi/\bar{V}_{\text{hyd}}) p \bar{V}_{\text{H}}| \ll |\Delta g'_{\text{chem}} - A_1 - cA_2|$ , we can approximate  $\Delta G_k$  by

$$\Delta G_k = \frac{2}{3} \pi \frac{\bar{V}_p^3}{[c(\Delta g'_{\text{chem}} - A_1 - cA_2)]^2} \left\{ 1 - \frac{2c[B - (\pi/\bar{V}_{\text{hyd}}) p \bar{V}_{\text{H}}]}{c(\Delta g'_{\text{chem}} - A_1 - cA_2)} \right\} \quad (10)$$

This can be written

$$\Delta G_k = \frac{2}{3} \pi \frac{\bar{V}_p^3}{[c(\Delta g'_{\text{chem}} - A_1 - cA_2)]^2} - \frac{4}{3} \pi \frac{c[B - (\pi/\bar{V}_{\text{hyd}}) p \bar{V}_{\text{H}}] \bar{V}_p^3}{[c(\Delta g'_{\text{chem}} - A_1 - cA_2)]^3} \quad (11)$$

In terms of the critical nucleus volume at zero stress,  $V_k^0 = \frac{4}{3} \pi c(a_k^0)^3$ ,



with  $a_k^0$  given by Equation (A.21) as

$$a_k^0 = \frac{\bar{v}_p}{c(\Delta S_{chem} - A_1 - \epsilon A_2)}$$

we obtain

$$\Delta G_k = \Delta G_k^0 - v_k^0 [B - (x/\bar{v}_{hyd}) p\bar{v}_H] \quad (12)$$

where  $\Delta G_k^0$  is the critical nucleus energy at zero external stress. The nucleation rate can, consequently, be written

$$J = J_0 \exp \left\{ v_k^0 [B - (x/\bar{v}_{hyd}) p\bar{v}_H] / kT \right\} \quad (13)$$

where  $J_0$  is the nucleation rate at zero external stress. Thus, the nucleation rate when external stresses are acting on the sample is simply the nucleation rate at zero stress modified by the exponential factor. A similar result was derived by Ellis [2] and Sauthoff [5] except for the term  $(x/\bar{v}_{hyd}) p\bar{v}_H$ , which was incorrectly omitted by both authors. Note that if the hydride misfit were isotropic and there were no additional strains in converting a solution of zirconium and hydrogen to hydride (i.e., the molar volumes of hydrogen in zirconium and hydride are the same), then the effect of a uniform stress would be zero. Thus, stress can only affect the nucleation if the hydride misfit is anisotropic (which it is) and/or if the molar volume of hydrogen in zirconium differs from that in hydride. Recent results [11] indicate that the latter condition may not be the case, and hence only the anisotropic component of the misfit contributes to the effect of stress on hydride nucleation. The potency of the effect of external stress on nucleation at a particular temperature thus depends on the magnitude of  $v_k^0$  and the term  $B - (x/\bar{v}_{hyd}) p\bar{v}_H$ . Large values of both quantities would enhance the orienting effect of stress during nucleation. The value of  $B - (x/\bar{v}_{hyd}) p\bar{v}_H$  is determined, in part, by the applied stress, whereas  $v_k^0$  is determined by the ease with which hydride precipitates can

nucleate. Favourable conditions (large undercooling, low interfacial energy and small strain energy) result in small values of  $v_k^0$ , which would tend to reduce the orienting efficiency of the nucleation stage.  $v_k^0$  is therefore critical in determining the orienting efficiency of the nucleation stage, and in the following section we present an analysis of relevant experimental data used to estimate this parameter.

### 2.3 ANALYSIS OF HYDRIDE PRECIPITATION DATA

In previous studies by Puls [8,9], it was argued that the terminal solid solubility (TSS), measured on cool-down from a temperature where all the hydrogen is in solution, determines the onset of hydride precipitation, i.e., the temperature (for a given hydrogen concentration) at which hydrides nucleate. It was further argued that the TSS determined on heat-up corresponds approximately to the stress-free, or chemical, solvus [9]. On the basis of these data, then, it is possible to calculate the undercooling from the stress-free, or chemical, solvus required to initiate nucleation. This information will now be used to determine parameters in the nucleation rate expressions given in the previous section.

It is evident from a study of Table 2 in reference 8 that there was a large variation in the undercooling, which appears to depend on the material on which the measurements were made. In the following we have restricted ourselves to only two of these, spanning the range from the largest to the smallest undercooling (see Table 1). We have also re-analyzed the data to take account of the temperature dependence of Young's modulus [15]. This leads to a temperature-dependent accommodation strain energy. The reanalysed data are presented in Table 2, which gives the undercooling from the constrained solvus. This provides the net chemical energy available for nucleation of an elastically constrained nucleus. We note that the inclusion of a temperature-dependent accommodation strain energy has resulted in more realistic undercooling values for zirconium, for which we had previously obtained unphysical negative values. In addition, for both materials, the decrease in  $\Delta T$  in going to higher temperatures is now less.

20 20 J/m<sup>2</sup> - 9 -

Table 3 summarizes the critical nucleation energies determined using the data from Tables 1 and 2. The largest uncertainty in these calculations comes from the estimates of the interfacial energies  $\gamma_1$  and  $\gamma_c$ . The choice of  $0.02 \text{ J/m}^2$  for  $\gamma_c$  is about as low as is physically reasonable for a coherent interface [10], thus placing a lower limit on this value. A reasonable estimate for  $\gamma_1$  is less certain, but the value chosen is assumed to be in the range applicable to homogeneous nucleation conditions. The calculations show that  $\gamma$ -hydrides have critical nucleus energies more than an order of magnitude lower, and would be favoured as the nucleating phase. With the assumption chosen, the lower nucleation energy for  $\gamma$ -hydrides is expected because of their lower strain energy compared to  $\delta$ -hydrides. Insertion of the  $\Delta G_k$  values into Equations (1) and (2) shows nonetheless that "homogeneous" nucleation for either phase is not possible. Since hydrides are, however, observed to form (although it is not always clear how they were nucleated), this result suggests that estimates for some of the physical constants are incorrect. (We assume the validity of the classical nucleation model).

The critical nucleation energy depends on the cube of the effective interfacial energy,  $\bar{\gamma}$ . Therefore  $\Delta G_k$  is a very sensitive function of  $\bar{\gamma}$ , and even small changes in  $\bar{\gamma}$  can have large effects on  $\Delta G_k$  and, hence, the nucleation rate. Thus, heterogeneous grain boundary nucleation, produced by lowering  $\bar{\gamma}$ , seems likely to dominate at small undercooling [10,16]. In addition, the reduction of  $\Delta G_{\text{strain}}$  by precipitation near dislocations or by the formation of a metastable phase with a lower strain energy can also increase the nucleation rate [16]. It was found that for the TSS data given in Table 3, lowering the value of  $\bar{\gamma}$  (by lowering  $\gamma_1$ ) is the most effective means of increasing the nucleation rate to the observable levels of, say,  $10^{12} \text{ nuclei/(m}^3 \cdot \text{s)}$ . Reduction of the strain energy term to negligible levels is, by itself, not sufficient to obtain an observable nucleation rate, except for the case of  $\gamma$ -hydrides in Alloy-2.

In Table 4 we have summarized the values of the interfacial energy and the resulting critical nucleus dimensions and energies that give an acceptable nucleation rate around  $10^{16} - 10^{17} \text{ nuclei/(m}^3 \cdot \text{s)}$ . These values are meant to reflect lower limits for the nucleation rate, and hence upper

TABLE 1

SUMMARY OF TSS DATA FOR HYDRIDES IN ZIRCONIUM AND ZIRCONIUM-2

limits for  $V_k^0$ . Higher nucleation rates would correspond to smaller values of  $V_k^0$ . Obviously, the choice of an acceptable nucleation rate is somewhat arbitrary, but fortunately large changes in this rate correspond to fairly small changes in  $V_k^0$ . Thus, our estimate of  $V_k^0$  is likely to be accurate within a factor of two. Note that to obtain acceptable nucleation rates from the data on pure zirconium, it was necessary to also reduce the strain energy of the nucleus by significant amounts. The analyses show that if  $\delta$ -hydrides are the nucleating phase, the values of  $V_k^0$  given in Table 4 range from  $2.6 \times 10^{-27}$  to  $5.5 \times 10^{-27} \text{ m}^3$ , whereas if  $\gamma$ -hydrides are the nucleating phase, the  $V_k^0$  values range from  $2.6 \times 10^{-27}$  to  $10.4 \times 10^{-27} \text{ m}^3$ .

#### 2.4 EFFECT OF EXTERNAL STRESS ON HYDRIDE NUCLEATION

In Section 2.2 we showed that when  $B - (x/\bar{V}_{\text{hyd}}) p\bar{V}_H$  is much smaller than the difference between the chemical free energy at zero stress and the accommodation strain energy terms, the nucleation rate under external stress can be approximated by Equation (13),

$$J = J_0 \exp\left\{V_k^0 [B - (x/\bar{V}_{\text{hyd}}) p\bar{V}_H] / kT\right\} \quad (13)$$

This relation can be used to determine the orienting efficiency due to external stress during the nucleation stage.

We wish to evaluate the results of tests done on samples cut from zirconium-based pressure tubes. To simplify the analysis, we assume that the crystallographic textures of the tubes are such that there are equal numbers of basal poles of the hexagonal-close-packed (hcp) Zr-matrix crystals pointing in the radial and tangential directions, and none in the longitudinal direction. We also assume that  $J \propto N$ , where  $N$  is the number of hydride precipitates observed, and that a uniaxial tensile stress is applied along the tangential pressure-tube direction. Hence,

$$N_a^0 = N_0 \exp\left\{V_k^0 [B_a - (x/\bar{V}_{\text{hyd}}) p\bar{V}_H] / kT\right\} \quad (14)$$

and

$$N_{na}^o = N_o \exp \left\{ v_k^o [B_{na} - (x/\bar{v}_{hyd}) p \bar{v}_H] / kT \right\} \quad (15)$$

where the subscripts a and na refer to "aligned" and "non-aligned" hydrides, respectively, as explained in Section 2.2. Defining

$$n = \frac{N_a^o}{N_a^o + N_{na}^o} \quad (16)$$

then  $n=1$  means complete alignment and  $n=1/2$  means random alignment, i.e., equal numbers of hydrides in the two orientations. Equation (16) can be written

$$n = \frac{1}{1 + \exp [v_k^o \Delta B / kT]} \quad (17)$$

where  $\Delta B = B_{na} - B_a$  and the isotropic term  $(x/\bar{v}_{hyd}) p \bar{v}_H$  has cancelled out. Multiplied by 100,  $n$  is equivalent to  $F$ , the percentage of hydrides whose trace is perpendicular to the applied stress.  $F$  is a constant that has been widely used in the literature [2] to characterize the hydride distribution.

As an application of Equation (17), we consider the case of an external uniaxial stress applied along the tangential (circumferential) direction of the pressure tube, with all other stresses equal to zero. The "aligned" hydrides are, therefore, those with their plate (or needle) normals in the tangential direction (radial hydrides), whereas the "non-aligned" hydrides are those with their plate (or needle) normals in the radial direction (circumferential hydrides). The results are summarized in Table 3 for a series of applied stresses, assuming that the hydrides in the sample are  $\beta$ -hydride plates lying on basal planes. The calculations show that even at an applied stress of 50 MPa, stress-orienting effects should be observable. However, rather complete orienting does not occur until

stresses of around 200 MPa are applied to the sample. It is also evident from Table 3 that there is not much difference in orienting tendency between hydrides in Zircaloy-2 and zirconium. Thus, it should be possible to observe a stress-orienting effect in zirconium if stresses around 100 MPa can be applied. This should be practical in zirconium containing sufficient amounts of dissolved oxygen, where the yield stress would be above 100 MPa [19].

The effect of a uniaxial stress on the orienting of  $\gamma$ -hydride needles is more complicated, and could be zero because of the various  $\langle 11\bar{2}0 \rangle$  directions that are available. That is, it depends on the orientation of the hydride's needle axis with respect to the applied stress, and on the grain orientation on which the hydride chooses to precipitate. The most favourable  $\gamma$ -hydride case, "non-aligned" hydrides with their needle axes parallel, and "aligned" hydrides with their axes perpendicular to the applied stress, gives a stronger orienting effect than does the most favourable  $\delta$ -hydride case, since the misfit difference involved (using the value derived by Carpenter [18]) is more than double that for  $\delta$ -hydride. The results of these calculations have also been summarized in Table 5.

In pressure-tube material, a fabrication procedure has been chosen that results in a preferential ("circumferential") orientation of the hydrides. The present analysis suggests that this preferred orientation is the result of internal stresses. As pointed out by Perovic et al. [20], "the sign of these stresses is such that the basal planes are either under compression in grains where the c-axis is nearly parallel to the circumferential direction or are under tension in those grains where the c-axis is nearly parallel to the radial direction". It is found experimentally that the stress required to reorient most of the hydrides from the circumferential to the radial direction in one cycle requires a tensile stress in the circumferential direction of about 400 MPa in cold-worked Zr-2.5 wt% Nb and about 200 MPa in Zircaloy-2 [21]. From the foregoing, assuming values of  $V^b$  for Zr-2.5 wt% Nb similar to Zircaloy-2, we calculate that in Zr-2.5 wt% Nb the magnitude of the internal stress is about 200 MPa. This would be sufficient to give a strongly aligned hydride distribution in externally unstressed material, as observed. The smaller applied stress values for a

$\bar{\epsilon}_h$ ( $10^{-2}$ )	1.346	1.346	1.346	1.449	1.449
	1.319	1.319	1.319	1.512	1.512
				1.649	1.649
				1.972	1.972

strong hydride reorientation effect in Zircaloy-2 suggests that internal stresses are much smaller in this material. According to Table 5, the internal stresses are likely to be less than 100 MPa. This is consistent with metallographic observations [21], which show that hydrides in Zircaloy-2 are less strongly aligned along the circumferential direction than those in Zr-2.5 wt% Nb.

### 3. GROWTH

Hydride growth refers to the stage after the hydride precipitates have formed (nucleated), but when there is still a supersaturation of hydrogen in solution. The difference between the hydrogen concentration in the (supersaturated) matrix far from the hydride and the equilibrium concentration near the hydride provides the driving force for growth.

The average concentration of hydrogen in the matrix in the vicinity of a hydride particle is given by [8]

$$C_H^{\sigma, \text{con}} = C_H^s \exp[\bar{V}_{\text{hyd}} \Delta \epsilon_{\text{strain}} / xRT] \exp[-\bar{V}_{\text{hyd}} B / xRT] \exp[p\bar{V}_H / RT] \quad (18)$$

where we have rewritten the expression given in reference 8 in the notation of the present paper.  $\Delta \epsilon_{\text{strain}}$ ,  $B$ ,  $\bar{V}_{\text{hyd}}$ ,  $\bar{V}_H$ ,  $x$  and  $RT$  are as defined in previous sections. The ratio of equilibrium concentrations for "aligned" and "non-aligned" hydrides in a sample subjected to an external stress is given by

$$\frac{C_H^{\sigma, \text{con}}(\text{na})}{C_H^{\sigma, \text{con}}(\text{a})} = \exp[-\bar{V}_{\text{hyd}} \Delta B / xRT] \quad (19)$$

For  $\delta$ -hydrides and the uniaxially applied stresses of 50-300 MPa considered in Table 5, the ratio  $C_H^{\sigma, \text{con}}(\text{na})/C_H^{\sigma, \text{con}}(\text{a})$  ranges from 1.00003 to 1.0002.

Thus, there would be a negligible difference due to external stress, between the driving forces for the growth of "aligned" and "non-aligned" hydrides, for applied stresses of practical interest.

#### 4. COARSENING

During particle coarsening the hydrogen concentration in the matrix is in the same range as the solubility of an individual hydride particle. The latter will depend on its size and orientation with respect to any applied stress. Large particles are favoured over smaller ones, and "aligned" particles over "non-aligned" ones. Sauthoff [5] has shown how to analyze such a situation and we follow his approach below.

By combining Equation (A.22) with Equation (A.6), an expression can be obtained for the solubility of a  $\delta$ -hydride precipitate as a function of its dimensions (particle radius  $a_1$ ), as follows:

$$\frac{xRT}{\bar{v}_{\text{hyd}}} \ln \frac{C_H^s(a_1)}{C_H^s} = -\frac{\bar{v}}{\epsilon \cdot a_1} + A_1 + \epsilon A_2 - B + (x/\bar{v}_{\text{hyd}}) p \bar{v}_H \quad (20)$$

From Equation (20), the ratio of the solubilities of two hydrides of identical orientations, but different radii  $a_1$  and  $a_2$ , is given by

$$\ln \frac{C_H^s(a_1)}{C_H^s(a_2)} = \frac{\bar{v}_{\text{hyd}}}{xRT} \frac{\bar{v}}{\epsilon} \left( \frac{1}{a_1} - \frac{1}{a_2} \right) \quad (21)$$

The particle size difference, for differently oriented hydrides, that would give no solubility difference is

$$\frac{\bar{v}}{\epsilon} \left( \frac{1}{a} - \frac{1}{a_{\text{na}}} \right) = -\Delta B \quad (22)$$



Defining

$$\epsilon = \frac{a_a}{a_{na}} \quad (23)$$

Equation (22) can be rewritten

$$-\frac{\epsilon \Delta B}{\bar{r}} = \frac{1}{a_a} (1-\epsilon) \quad (24)$$

This relation shows that an "aligned" particle of radius  $a_a$  has the same solubility (and therefore grows or shrinks at the same rate) as a "non-aligned" particle with radius  $a_{na}$  ( $>a_a$ ). The constant  $\epsilon$  could, therefore, be considered an equivalent radius ratio, as it adjusts the size of the "aligned" particles to bring them to the same size scale as the "non-aligned" particles. That is, by setting

$$a_a(\text{adj}) = \frac{a_a}{\epsilon}$$

where  $a_a(\text{adj})$  is the adjusted "aligned" particle radius, these adjusted particles can now be dealt with in the same way as the radii of the "non-aligned" particles, in investigating the coarsening kinetics.

During coarsening, the biggest particles grow fastest, whereas those having the mean radius, which is about half the maximum, are about to stop growing. Thus, choosing  $\epsilon = 1/2$ , Equation (24) defines a minimum mean radius for a situation where even the biggest "non-aligned" hydrides will not grow any more. As an example, at an applied stress of 200 MPa, and choosing  $T = 367$  K and  $\bar{\gamma} = 0.041$  J/m<sup>2</sup> ( $\gamma_s = 0.075$  J/m<sup>2</sup>,  $\epsilon = 0.14$ ), Equation (24) tells us that, when the mean particle radius for the distribution is  $> 2.794 \times 10^{-8}$  m, all "non-aligned" particles would stop growing. ) *dup?*

To achieve complete orienting in the pressure-tube materials considered in the previous sections, all the "non-aligned" particles (half the total particles) would have to disappear, plus half the "aligned" ones. This factor-of-four decrease in the total number of precipitates means that

we require an increase in the mean particle radius by a factor  $4^{1/3} = 1.6$ . Thus, an increase by 60% of the mean particle radius will result in complete orienting of the particles under the influence of the stress, provided the particles are large enough, as given by Equation (24). If coarsening occurs during an earlier precipitation stage, where the mean radius is smaller than that given above, then, from Equation (24),  $\tau$  will be larger than  $1/2$ , and more hydrides will have to dissolve to achieve complete orienting. This will, in turn, mean that the mean radius will have to increase by more than 60% for complete orienting.

To determine the time in which complete orienting can occur, an equation for the rate of increase of particle size during coarsening is required. Boyd and Nicholson [22] have derived such an expression for disc-shaped particles, based on the Lifshitz-Wagner solute diffusion-controlled coarsening theory. They obtained the following expression for the increase in the mean particle radius  $\bar{a}$  with time  $t$ :

$$\bar{a}^3 - \bar{a}_0^3 = \frac{t - t_0}{\tau} \quad (25)$$

with 
$$\frac{1}{\tau} = \frac{16}{9} \frac{\gamma_H D_H C_H^s \bar{V}_{hyd}}{c_H k T}$$

It is evident from Equation (25) that the coarsening rate is both a sensitive function of the mean particle radius (it increases as the cube of that radius) and the temperature at which the coarsening takes place (it decreases exponentially with temperature, through  $D_H C_H^s$ ). Therefore, large mean particle radii and/or low holding temperatures can result in negligible coarsening rates.

For the example chosen above,  $\tau = 1.272 \times 10^{21} \text{ s}^{-1}$ ; therefore to increase the minimum mean particle radius of  $2.794 \times 10^{-8}$  by a factor of 1.6 would take less than a second at 567 K. Therefore, reorientation by coarsening would be possible for such small hydride particle sizes. To obtain such small sizes, however, would be rather difficult experimentally,

as the sample would have to be held at just below the nucleation temperature, and this temperature is not known accurately. Moreover, as examination of the precipitate distribution is generally carried out at room temperature, the final result could be obscured by subsequent additional nucleation and growth steps. More realistic holding temperatures and larger particle sizes give negligible coarsening rates, as summarized in Table 6.

### 5. DISCUSSION AND CONCLUSIONS

The foregoing analysis shows that the preferential orientation of hydride precipitates under stress is most efficient during the nucleation stage. The reason for this is that the overall driving force for nucleation, for the parameters and conditions chosen, is fairly small and therefore the driving force for orienting under stress can be a substantial fraction of the overall force. The analysis shows that hydride growth is unlikely to play a role in preferential orientation, but coarsening could be important under carefully chosen experimental conditions. However, in the standard stress reorientation tests, where a sample is heated to above the TSS and then cooled to room temperature under stress, only the nucleation stage is likely to be effective in reorienting hydrides. It should be noted that the present treatment has been highly simplified and contains a number of unsupported physical assumptions.

The foremost assumption is the validity of homogeneous and heterogeneous classical nucleation theory, i.e., that nucleation proceeds via a thermally activated critical clustering process. Such a theory may not be strictly applicable to the formation of precipitates involving structural as well as compositional modifications, such as is the case for zirconium hydrides. It has been postulated [23,24,25] that the structural aspect of the formation of zirconium hydrides is similar to a martensitic type of transformation involving the shearing of the hcp lattice. Classical nucleation theory may not be applicable to such structural transformations, as has been found for the nucleation of martensite

where  $p$  is the hydrostatic stress, and  $\bar{V}_H$  the molar volume of hydrogen in zirconium. To simplify the subsequent expressions, we drop the superscript

[26,27]. Moreover, there are recent suggestions [20] that many of the hydrides nucleate near existing ones, in an autocatalytic fashion. The quantitative implications of these mechanistic details have not been considered in the present treatment.

In addition to these difficulties, a large uncertainty in the application of the classical nucleation theory involves the choice of the interfacial energies,  $\gamma_i$  and  $\gamma_c$ . As previously stated, the critical nucleation energy, and hence the critical nucleus volume, is a very sensitive function of the assumed interfacial energies. Based on the transformation mechanism postulated by Carpenter [24] and Weatherly [25], and the experimentally observed shapes of the hydrides, it seems reasonable to assume that the flat faces of the plate and the circular faces of the needle form coherent or semicoherent interfaces, whereas the edges or ends, respectively, form incoherent interfaces. Choosing a very low value for  $\gamma_c$ , we have adjusted the value for  $\gamma_i$  to give an acceptable minimum nucleation rate. This has necessitated choosing fairly low values for  $\gamma_i$ . We have, unfortunately, no independent way to determine whether the values chosen are reasonable for zirconium hydrides.

Other quantities that determine the critical nucleus in an important way are the chemical driving force and the accommodation and interaction energies. The chemical driving force depends on the correct choice of the nucleating temperature. We have determined this indirectly from experimental data on the cooling solvi measured by dilatometry. There is a certain amount of scatter in these data as well as in the corresponding heating solvi, and this will be reflected by some uncertainty in the calculated value of  $\Delta G_{chem}$ .

Possibly important uncertainties in the estimates of the accommodation and interaction energies are the values of the misfit or transformation strains. We have chosen to use those determined by Carpenter [18], based on the difference in the crystal structure of the hydrides and the zirconium matrix. Somewhat different values for  $\gamma$ -hydrides were deduced more recently [24], based on detailed arguments on the mechanism of  $\gamma$ -hydride formation. A significant misfit component

constant eccentricity, by writing the volume of the precipitate in terms of  $c$  and solving

emerging from this analysis, not considered in the previous study [18], is a large shear misfit. However, inclusion of a large shear strain into the expression for the accommodation strain energy results in very large strain energies. On the other hand, our recent analysis [9] shows that the calculated values, based on the misfit strains deduced by Carpenter [18], appear to be reasonable. Perovic et al. [20] have also suggested that  $\delta$ -hydrides may form with a shape change similar to that of a martensitic transformation. They assume that all of the 17% volume misfit may be accommodated along the plate normal, while in addition there is a large shear parallel to the habit plane. Using these latter transformation strains, an accommodation strain energy is obtained that is close to the value obtained based on Carpenter's strains [18]. However, there would be an enormous difference in the orienting tendencies of the hydrides, depending on which set of transformation strains is used. The values suggested by Perovic et al. would give a significantly higher orienting energy (by a factor of more than six) under the influence of a uniaxial stress.

The recent study by Puls [9] shows that there is a close relationship between the observed hysteresis in the TSS and the accommodation strain energy. Therefore, despite some uncertainties in the chosen transformation strains, the strain energies used in the present analysis appear to be fairly reliable. This leaves only the interfacial energies as uncertain parameters, and these we were able to determine by requiring that the model must give an observable nucleation rate, in agreement with the indirect experimental observations.

According to Equations (13) and (17), stress orientation during nucleation is enhanced when the critical nucleus volume is large. This is possible when i) the driving force for nucleation is small (i.e., small undercooling from the solvus, which is likely to occur during slow cooling), ii) the applied stresses are high and, iii) there is a large transformation strain anisotropy. As the transformation strain anisotropy is larger for  $\gamma$ -hydrides as opposed to  $\delta$ -hydrides, the former should exhibit a stronger orienting effect, assuming that they can be formed at slow cooling rates.

$$c_k = \frac{\gamma_c}{(\Delta\epsilon - \Delta\epsilon_c) - \gamma} - \frac{\gamma_1}{2\Delta}$$

A feature of stress orienting during the nucleation stage is that, provided the applied stresses are high enough, complete orienting should not occur unless all the hydrides have been dissolved. This was confirmed experimentally by Hardie and Shanahan [28], thus providing an important test of the conclusion that orienting is governed by the nucleation stage. By assuming that hydride orientation would follow a dependence given by Equation (17), and fitting this to their experimental results, they deduced that the average value for the exponential term divided by the applied uniaxial tensile stress was  $4.6 \times 10^{-8} \text{ m}^2/\text{N}$ . Assuming a nucleation temperature of 573 K at a hydrogen concentration of 100  $\mu\text{g/g}$  and a net misfit of 0.0262, we obtain a value of  $13.883 \times 10^{-27} \text{ m}^3$  for  $V_k^0$ . (Hardie and Shanahan [28] obtained a value of  $7.450 \times 10^{-27} \text{ m}^3$  assuming a larger net misfit of 0.05.) The  $V_k^0$  value obtained from the experimental fit is about a factor of two larger than the estimated value given in Table 5. This agreement seems reasonable in view of the uncertainties mentioned in estimating the nucleation parameters and the misfit strains, and the difficulties in determining the internal stresses in the samples used.

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**TABLE 1**  
**SUMMARY OF TSS DATA FOR HYDROGEN IN ZIRCONIUM AND ZIRCALOY-2,**  
**USED TO DETERMINE THE CHEMICAL FREE ENERGY FOR NUCLEATION**

Reference	Material	Method	Temperature Range (K)	Constants A Q (kJ/mol)
Kearns [12]	Zircaloy-2 and -4	Diffusion equilibrium (heating)	533-798	11.50 34.54
Kearns [12]	Zirconium	Diffusion equilibrium (heating)	533-798	11.78 36.47
Erickson and Hardie [13]	Zirconium	Dilatometry (cooling)	373-671	11.48 32.45
Slattery [14]	Zircaloy-2	Dilatometry (cooling)	436-563	10.34 25.15

† The data have been represented in the form of an Arrhenius equation:  
 $\ln C_H = A - Q/RT$ ;  $C_H$  = hydrogen concentration ( $\mu\text{g/g}$ );  $T$  = temperature (K);  
 $R$  = gas constant.

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**TABLE 2**  
**VALUES OF UNDERCOOLING FROM THE CONSTRAINED SOLVUS DERIVED FROM**  
**THE TSS DATA (SUMMARIZED IN TABLE 1) FOR ZIRCONIUM AND ZIRCALOY-2†**

Reference	Material	Hydride Type	$\bar{C}_H$ ( $\mu\text{g/g}$ )	$\Delta T$ (K)
Erickson and Hardie [13]	Zirconium	$\delta$	100	6
		$\delta$	400	5
		$\gamma$	100	10
		$\gamma$	400	10
Slattery [14]	Zircaloy-2	$\delta$	35	41
		$\delta$	150	32
		$\gamma$	35	45
		$\gamma$	150	37

† Using  $E = 97.08 - 0.058(T-273)$  GPa [15],  $\nu = 0.3$ , and the strain energies calculated by means of Equations (A.4) and (A.25). The numerical values of the strain energies used are given in Table 3. The final values have been reduced by 10% as in reference 8 to take account of possible non-linear effects.

**TABLE 3**  
**CRITICAL HOMOGENEOUS NUCLEATION ENERGIES**  
**FOR  $\delta$ - AND  $\gamma$ -HYDRIDES IN ZIRCALOY-2 AND ZIRCONIUM**

Material	$T_n$ (K)	Hydride Type	$\Delta G_{chem}$	$\Delta G_{strain}^\dagger$		$\Delta G_k^\#$ (J)
				$A_1$	$A_2$	
Zircaloy-2	567	$\delta$	4.020	2.290	2.278	$2.578 \times 10^{-17}$
		$\gamma$	2.514		1.283	$1.194 \times 10^{-19}$
	446	$\delta$	5.176	2.766	2.753	$1.317 \times 10^{-17}$
		$\gamma$	3.237		1.396	$5.339 \times 10^{-19}$
Zirconium	711	$\delta$	2.301	1.929	1.919	$6.595 \times 10^{-16}$
		$\gamma$	1.439		1.081	$1.412 \times 10^{-17}$
	568	$\delta$	2.637	2.206	2.195	$4.900 \times 10^{-16}$
		$\gamma$	1.649		1.236	$1.061 \times 10^{-17}$

# Assuming  $\gamma_1 = 0.8 \text{ J/m}^2$ ,  $\gamma_c = 0.02 \text{ J/m}^2$

† See footnote to Table 2

**TABLE 4**  
**VALUES OF SOME PHYSICAL CONSTANTS AND CRITICAL NUCLEI DIMENSIONS**  
**THAT GIVE ACCEPTABLE NUCLEATION RATES AT ZERO EXTERNAL STRESS**

Material	T <sub>m</sub> (K)	Hydride Type	$\gamma_i$ (J/m <sup>2</sup> )	$c_k^0$ (10 <sup>-10</sup> m)	$a_k^0$ (10 <sup>-9</sup> m)	$\epsilon^0$	$\Delta G_k^0$ (10 <sup>-19</sup> J)	$\Delta G_k^0/T$ (10 <sup>-22</sup> J/K)	$J^{00}$ (nuclei/m <sup>3</sup> ·s)	$v_k^0$ (10 <sup>-27</sup> m <sup>3</sup> )	$D_H^{00}$ (10 <sup>-10</sup> m <sup>2</sup> /s)	$\bar{c}_H$ (10 <sup>-2</sup> )
Zircaloy-2	567	δ	0.075	2.924	2.071	0.14	3.700	6.526	8.602x10 <sup>16</sup>	5.253	1.267	1.368
	446	δ	0.095	2.169	1.678	0.13	2.628	5.867	2.117x10 <sup>17</sup>	2.559	0.1753	0.319
	567	γ	0.2	4.874	5.734	0.085	3.512	6.194	5.225x10 <sup>16</sup>	5.706	1.267	1.368
	446	γ	0.364	3.259	5.926	0.055	2.427	5.533	1.105x10 <sup>17</sup>	2.636	0.1753	0.319
Zirconium	711	δ	0.075*	3.08	2.072	0.15	3.806	5.353	2.655x10 <sup>17</sup>	5.548	5.724	3.649
	568	δ	0.085*	2.721	1.969	0.14	3.532	6.218	4.789x10 <sup>17</sup>	4.419	1.267	0.912
	711	γ	0.166†	6.678	5.565	0.12	4.700	6.568	7.900x10 <sup>16</sup>	10.395	5.724	3.649
	568	γ	0.166‡	5.820	4.850	0.12	3.547	6.244	3.464x10 <sup>16</sup>	6.880	1.267	0.912

\* A<sub>1</sub> reduced by 2/3 from value given in Table 3.

† A<sub>g strain</sub> reduced by 1/2 from value given in Table 3.

‡ Using  $N_0 = 4.325 \times 10^{28}$  sites/m<sup>3</sup>,  $d = 4.5 \times 10^{-10}$  m

§ Using  $D_H = 2.17 \times 10^{-7} \exp[-35,100/RT]$  m<sup>2</sup>/s [17].

**TABLE 5**  
**EFFECT OF A UNIAXIAL EXTERNAL TENSILE STRESS ON THE ORIENTING TENDENCY**  
**OF  $\gamma$ - AND  $\delta$ -HYDRIDES DURING NUCLEATION, USING THE HYDRIDE MISFIT STRAINS**  
**DETERMINED BY CARPENTER [18]**

Material:	Zircaloy-2		Zircaloy-2		Zirconium		Zirconium	
$T_n$ (K):	367	367	448	448	711	711	568	568
$v_k^0$ ( $10^{-27} m^3$ ):	5.253	5.706	2.559	2.636	5.548	10.395	4.419	6.880
Hydride Type:	$\delta$	$\gamma$	$\delta$	$\gamma$	$\delta$	$\gamma$	$\delta$	$\gamma$
$\sigma^A$ (MPa)			n					
50	0.707	0.888	0.632	0.771	0.677	0.953	0.677	0.924
100	0.853	0.985	0.747	0.919	0.815	0.998	0.814	0.993
150	0.933	0.998	0.836	0.975	0.902	1.000	0.902	0.999
200	0.971	1.000	0.897	0.992	0.951	1.000	0.951	1.000
250	0.988	1.000	0.938	0.998	0.976	1.000	0.976	1.000
300	0.995	1.000	0.963	0.999	0.988	1.000	0.988	1.000

**TABLE 6**  
**TIME,  $\Delta t$ , TO INCREASE THE INITIAL MEAN  $\delta$ -HYDRIDE RADIUS**  
 **$\bar{a}_0$  BY 60% DURING COARSENING**

T (K)	$C_H^s$ (atomic fraction)	$D_H$ ( $m^2/s$ )	$\tau$ (s)	$\bar{a}_0$ (m)	$\Delta t$ (s)
448	$8.455 \times 10^{-4}$	$1.753 \times 10^{-11}$	$5.086 \times 10^{22}$	$1 \times 10^{-6}$	$1.526 \times 10^5$
373	$1.310 \times 10^{-4}$	$2.636 \times 10^{-12}$	$1.817 \times 10^{24}$	$1 \times 10^{-6}$	$5.45 \times 10^6$
300	$8.716 \times 10^{-6}$	$1.678 \times 10^{-13}$	$3.451 \times 10^{26}$	$1 \times 10^{-6}$	$1.035 \times 10^9$

APPENDIX A

EXPRESSIONS FOR THE CRITICAL NUCLEATION ENERGY  
FOR DELTA AND GAMMA HYDRIDE PRECIPITATES

A. Delta Hydrides

We assume that the  $\delta$ -hydrides precipitate as discs on the basal plane of the hcp zirconium lattice. For the purpose of calculating the strain energy, the plate is approximated by an oblate spheroid with major axis  $a$  and minor axis  $c$ . To simplify the calculation for the total interfacial energy, it is convenient to consider the plate as a disc of radius ' $a$ ' and thickness ' $2c$ '. It is then assumed that the face of the disc is coherent with the matrix, with a specific interfacial energy  $\gamma_c$ , whereas the sides are incoherent, with a specific interfacial energy  $\gamma_l$ . The total free energy for nucleation,  $\Delta G$ , for the oblate spheroid having volume  $V_{\text{plate}} = 4/3 \pi a^2 c$  is given by

$$\Delta G = \frac{4}{3} \pi a^2 c (\Delta g_{\text{strain}} + \Delta g_{\text{int}} - \Delta g_{\text{chem}}^{\delta}) + 2\pi a^2 \gamma_c + 4\pi a c \gamma_l \quad (\text{A.1})$$

where  $\Delta g_{\text{chem}}$  is the absolute value of the Gibbs free energy of transformation per unit volume, excluding strain energy contributions (the chemical free energy), and  $\Delta g_{\text{strain}}$  and  $\Delta g_{\text{int}}$  are the self-strain and interaction energies per unit volume, respectively. In the notation of I,

$$\Delta g_{\text{strain}} = \bar{W}_t^{\text{inc}} / \bar{V}_{\text{hyd}} \quad (\text{A.2})$$

$$\Delta g_{\text{int}} = \bar{G}_t^{\delta} / \bar{V}_{\text{hyd}} \quad (\text{A.3})$$

The strain energies  $\Delta g_{\text{strain}}$  and  $\Delta g_{\text{int}}$  have been evaluated in I. For  $c/a \ll 1$ ,  $\Delta g_{\text{strain}}$  is given by

$$\Delta g_{\text{strain}} = \frac{E}{1-\nu} A^2 + \frac{E}{1-\nu} \frac{\pi}{2} \frac{c}{a} (A \cdot \epsilon + \frac{1}{4(1+\nu)} \epsilon^2 + \frac{1}{8} \frac{(2-\nu)}{(1+\nu)} s^2) \quad (\text{A.4})$$

where  $E$  is Young's modulus,  $\nu$  is Poisson's ratio and  $A$  is the isotropic misfit strain;  $\epsilon$  is the misfit strain, in addition to  $A$ , in the direction of the plate normal; and  $s$  is the shear misfit in the plane of the plate. As shown in I,  $\Delta g_{\text{int}}$  depends on the applied stress. As an example, taking the simplest specific case of a uniaxial tensile stress,  $\sigma_{11}$ , applied in the direction of the plate-face normal, one obtains

$$\Delta g_{\text{int}} = - (A + \epsilon) \sigma_{11} \quad (\text{A.5})$$

The chemical free energy for delta hydrides is given by

$$\Delta g_{\text{chem}}^{\delta} = \frac{\pi}{\bar{v}_{\text{hyd}}^{\delta}} RT_n \ln \left( \frac{\bar{C}_H}{C_H^{\sigma}} \right) \quad (\text{A.6})$$

where  $\bar{v}_{\text{hyd}}^{\delta}$  is the molar volume of  $\delta$ -hydrides of composition  $\text{ZrH}_x$ , with  $x=1.66$  for  $\delta$ -hydrides;  $C_H^{\sigma}$  is the solubility of hydrogen in an externally stressed matrix in equilibrium with stress-free hydrides;  $\bar{C}_H$  is the solubility of hydrogen in the supersaturated matrix;  $T_n$  is the nucleation temperature, and  $R$  is the gas constant. It is assumed that the matrix is dilute in solute and that the nucleus has the composition given by the equilibrium phase diagram. The concentration  $C_H^{\sigma}$  in the externally stressed solid is given in terms of  $C_H^s$ , the hydrogen concentration in the unstressed matrix (approximately given by the heat-up TSS [A.1]), by

$$C_H^{\sigma} = C_H^s \exp[p\bar{v}_H/RT]$$



where  $p$  is the hydrostatic stress, and  $\bar{V}_H$  the molal volume of hydrogen in zirconium. To simplify the subsequent expressions, we drop the superscript  $\delta$  in the following development.

To determine  $\Delta G_k$ , the value for the critical nucleus in equilibrium with the supersaturated matrix, it is necessary to find the maximum of  $\Delta G$  as a function of  $c$  and  $a$ . In the following, we write the strain energy in the form

$$\Delta G_{\text{strain}} = A_1 + \frac{c}{a} A_2 \quad (\text{A.7})$$

and derive a number of approximate solutions.

The simplest approximate solution is obtained by assuming that

$$\Delta G_{\text{strain}} = A_1 \quad \left( A_1 = \frac{E}{1-\nu} a^2 \right) \quad (\text{A.8})$$

This is reasonable, as long as  $c/a \ll 1$  and  $A_2 \leq A_1$ . Taking the derivatives

$$\left( \frac{\partial \Delta G}{\partial a} \right)_c = 0 \quad \text{and} \quad \left( \frac{\partial \Delta G}{\partial c} \right)_a = 0 \quad (\text{A.9})$$

and solving for the critical radii  $a_k$  and  $c_k$  yields

$$a_k = \frac{3\gamma_i}{(\Delta G_{\text{chem}} - A_1 - \Delta G_{\text{int}})} \quad \text{and} \quad c_k = \frac{3\gamma_c}{(\Delta G_{\text{chem}} - A_1 - \Delta G_{\text{int}})} \quad (\text{A.10})$$

$$\text{Thus} \quad c = c_k/a_k = \gamma_c/\gamma_i \quad (\text{A.11})$$

and the eccentricity of the plate is independent of particle dimension, and is determined solely by the ratio of the surface energies. This is as expected in this approximation, where the strain energy is not explicitly shape dependent. It is convenient to obtain a solution in terms of the

constant eccentricity, by writing the volume of the precipitate in terms of  $c$  and solving

$$\left(\frac{\partial G}{\partial a}\right)_c = 0 \quad (A.12)$$

This yields

$$a_k = \frac{\bar{v}_p}{c(\Delta g_{\text{chem}} - A_1 - \Delta g_{\text{int}})} \quad (A.13)$$

for the critical radius, with

$$\bar{v}_p = v_c + 2c \cdot v_1 \quad (A.14)$$

and  $c$  given by Equation (A.11). The critical nucleation energy,  $\Delta G_k$ , is therefore

$$\Delta G_k = \frac{2}{3} \pi \frac{\bar{v}_p^3}{[c(\Delta g_{\text{chem}} - A_1 - \Delta g_{\text{int}})]^2} \quad (A.15)$$

A more accurate solution can be obtained by including the  $c/a$  term in  $\Delta g_{\text{strain}}$ . According to Equations (A.4) and (A.7),

$$A_2 = \frac{E}{1-\nu} \frac{\pi}{2} \left[ A_1 \epsilon + \frac{1}{4(1+\nu)} \epsilon^2 + \frac{1}{8} \frac{(2-\nu)}{(1+\nu)} \epsilon^2 \right] \quad (A.16)$$

with  $A_1$  given by Equation (A.8). The total free energy of nucleation is

$$\Delta G = -\frac{4}{3} \pi a^2 c (\Delta g_{\text{chem}} - \Delta g_{\text{int}} - A_1) + \frac{4}{3} \pi a c^2 A_2 + 2 \pi a^2 v_c + 4 \pi a c v_1 \quad (A.17)$$

Taking the derivatives as before (Equation (A.9)), and solving for the critical dimensions  $a_k$  and  $c_k$ , yields:

$$c_k = \frac{\gamma_c}{(\Delta g_{chem} - A_1 - \Delta g_{int})} - \frac{\gamma_1}{2A_2} \quad (A.18)$$

$$+ \left[ \frac{\gamma_1^2}{4A_2^2} + \frac{2\gamma_c\gamma_1}{(\Delta g_{chem} - A_1 - \Delta g_{int})A_2} + \frac{\gamma_c^2}{(\Delta g_{chem} - A_1 - \Delta g_{int})^2} \right]^{1/2}$$

$$a_k = \frac{3\gamma_1 + 2A_2c_k}{(\Delta g_{chem} - A_1 - \Delta g_{int})} \quad (A.19)$$

with the critical nucleation energy given by

$$\Delta G_k = -\frac{4}{3} \gamma_k^2 c_k (\Delta g_{chem} - A_1 - \Delta g_{int} - cA_2) + 2\gamma_k^2 \bar{\gamma}_p \quad (A.20)$$

Clearly, Equation (A.20) is not as transparent as the more approximate relation given by Equation (A.15).

A more transparent approximate expression can be obtained if we assume a size-independent eccentricity, as in the previous case. This gives

$$a_k = \frac{\bar{\gamma}_p}{c(\Delta g_{chem} - A_1 - \Delta g_{int} - cA_2)} \quad (A.21)$$

and

$$\Delta G_k = \frac{2}{3} \gamma_k^3 \frac{\bar{\gamma}_p^3}{[c(\Delta g_{chem} - A_1 - \Delta g_{int} - cA_2)]^2} \quad (A.22)$$

with  $\bar{\gamma}_p$  defined by Equation (A.14). The above result differs from Equations (A.13) and (A.14) only by the addition of the  $cA_2$  term. Note that with  $c$  determined from the solutions for  $c_k$  and  $a_k$  given by Equations (A.18-A.19), Equation (A.21) is equivalent to Equation (A.19), and Equation (A.22) to Equation (A.20).

## A.2 Gamma Hydrides

We assume that the  $\gamma$ -hydrides precipitate as needles, with their long axes along the  $\langle 11\bar{2}0 \rangle$  direction of the zirconium matrix. For the purpose of calculating the strain energy, the needle is approximated by a prolate spheroid with minor axis  $c$  and major axis  $a \gg c$ . To calculate the interfacial energy, the needle is approximated as a cylinder of length  $2a$  and radius  $c$ . We assume that the surface of the cylinder is coherent with the matrix and has a specific interfacial energy  $\gamma_c$ , whereas the two end faces are incoherent and have a specific interfacial energy  $\gamma_i$ . The total free energy for nucleation,  $\Delta G$ , for the prolate spheroid of volume  $V = 4/3 \pi c^2 a$  is then given by

$$\Delta G = \frac{4}{3} \pi c^2 a (\Delta G_{\text{strain}} + \Delta G_{\text{int}} - \Delta G_{\text{chem}}^{\gamma}) + 4\pi a c \gamma_c + 2\pi c^2 \gamma_i \quad (\text{A.23})$$

where

$$\Delta G_{\text{strain}} = \bar{v}_c^{\text{inc}} / \bar{v}_{\text{hyd}} = \frac{\pi}{1-\nu} \left\{ \frac{a^2}{2(1+\nu)} \right\} \quad (a \gg c) \quad (\text{A.24})$$

$$\Delta G_{\text{chem}}^{\gamma} = \frac{\pi R T}{\bar{v}_{\text{hyd}}} \ln \left( \frac{\bar{C}_H}{C_H^0} \right) \quad (\text{A.25})$$

$\bar{v}_{\text{hyd}}^{\gamma}$  = molar volume of  $\gamma$ -hydrides of composition  $\text{ZrH}_x$

$$x = 1$$

and all other symbols are as for the  $\delta$ -hydride case and are defined in I. Following the same procedure as for the  $\delta$ -hydrides, the critical dimensions are (to simplify the expressions, we drop the superscript  $\gamma$  in all of the following)

$$c_k = \frac{3\gamma_c}{(\Delta G_{\text{chem}} - \Delta G_{\text{strain}} - \Delta G_{\text{int}})} \quad (\text{A.26})$$

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$$\frac{\gamma_c}{\Delta A_1 - \Delta G_{int}} - \frac{\gamma_1}{2A_2} \quad (A.18)$$

$$\left[ \frac{2\gamma_c \gamma_1}{(\Delta G_{chem} - A_1 - \Delta G_{int}) A_2} + \frac{\gamma_c^2}{(\Delta G_{chem} - A_1 - \Delta G_{int})^2} \right]^{1/2} + \frac{2A_2 c_k}{\Delta A_1 - \Delta G_{int}} \quad (A.19)$$

nucleation energy given by

$$\frac{1}{2} c_k^2 (\Delta G_{chem} - A_1 - \Delta G_{int} - c A_2) + 2 \gamma_c \gamma_1 \bar{v}_p \quad (A.20)$$

(A.20) is not as transparent as the more approximate equation (A.15).

A transparent approximate expression can be obtained if we neglect eccentricity, as in the previous case. This

$$\frac{\bar{v}_p}{\Delta A_1 - \Delta G_{int} - c A_2} \quad (A.21)$$

$$\frac{\bar{v}_p^3}{[c(\Delta G_{chem} - A_1 - \Delta G_{int} - c A_2)]^2} \quad (A.22)$$

Equation (A.14). The above result differs from (A.14) only by the addition of the  $c A_2$  term. Note that from the solutions for  $c_k$  and  $a_k$  given by Equations (A.21) is equivalent to Equation (A.19), and Equation (A.20).

## A.2 Gamma Hydrides

We assume that the  $\gamma$ -long axes along the  $\langle 11\bar{2}0 \rangle$  direction. For the purpose of calculating the strain energy of a prolate spheroid with minor axis  $a$  and major axis  $b$ , the interfacial energy, the needle radius  $c$ . We assume that the matrix and has a specific free energy for nucleation,  $\Delta G = 4/3 \pi c^2 a$  is then given by

$$\Delta G = \frac{4}{3} \pi c^2 a (\Delta G_{strain})$$

where

$$\Delta G_{strain} = \frac{\bar{v}_{inc}}{\bar{v}_{hyd}} \bar{v}_{hyd}$$

$$\Delta G_{chem}^Y = \frac{xRT}{\bar{v}_{hyd}} \ln \left( \frac{\bar{c}}{c} \right)$$

$$\bar{v}_{hyd}^Y = \text{molal volume}$$

$$x = 1$$

and all other symbols are as before. Following the same procedure as in (A.14) to (A.19) (to simplify the expressions following)

$$c_k = \frac{3\gamma_c}{(\Delta G_{chem} - \Delta G_{strain})}$$