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Stability of β-85 wt% Nb precipitates in pressure tubes

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Cover picture: Post-test crucible microstructure; – 3-min, 2000°C/O-free Zry sample showing U-metal bridges (U) across cooling crack and contact with α-Zr(O) phase (Z). Fig. 4b from paper by P.J. Hayward and I.M. George on pages 43–52 of this issue.

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The analysis of bcc β-85 wt% Nb precipitate stability in pressure tubes of in-service nuclear reactors is performed here. The internal stresses generated by irradiation growth and creep processes and their influence on the anisotropy of the diffusion of vacancies and interstitials, are explicitly included in calculations. A slightly anisotropic shape of precipitates is predicted.

1. Introduction

The textured polycrystals of Zr–2.5 wt% Nb alloy that compose the pressure tubes of CANDU reactors, change their shape by irradiation growth and creep [1]. The individual grain distortion is restricted by the geometrical boundaries provided by neighboring grains. Internal stresses are generated which allow the distortion to be accommodated via elastic-plastic and creep deformation within each grain [2,3]. The strain of the lattice has an effect on the thermal migration of vacancies and interstitials produced by irradiation outside thermal equilibrium, and modifies the anisotropy of their diffusivity tensors [4,5]. These vacancies and interstitials may be trapped by other defects like dislocations [6], grain boundaries [7] and interfaces [8,9]. Also, both vacancies and interstitials may coprecipitate with solute atoms to form precipitates, and may affect their growth and stability (for a review see ref. [10]). This trapping at sinks of the former [11,12] and the growth and stability of precipitates [13], depend also on the anisotropy and therefore, on the strain of the lattice. Hence, the effect of the latter must be introduced in any theory which studies the stability of precipitates in an irradiated and stressed matrix.

Maydet and Russell's theory [14] briefly described in section 2 is adequate to take this effect into account. This theory was used in ref. [13] to analyze the stability of the initially cubic bcc β-85 wt% Nb particles in an unstrained hcp α-Zr (1 wt% Nb) matrix of the Zr–2.5 wt% Nb system, with a microstructure similar to the microstructure of the pressure tubes, under irradiation. An anisotropic shape of precipitates was predicted with the smaller dimension in the ***c***-hexagonal crystal direction. This predicted anisotropic shape was a direct consequence of including explicitly the anisotropy of the diffusion of vacancies and interstitials in the calculations. This anisotropy came from the intrinsic anisotropy of the hcp α-Zr lattice.

The same theory of Maydet and Russell will be used in this paper to analyze the bcc β-85 wt% Nb precipitates stability in the irradiated and external stressed hcp α-Zr (1 wt% Nb) matrix of the Zr–2.5 wt% Nb alloy of textured pressure tubes. The evolution of the elastic strain generated by the evolution of internal stresses, the additional anisotropy that they introduce on the diffusivity of the vacancies and interstitials, and consistently, the evolution of the total (intrinsic and additional) diffusivity anisotropy of vacancies and interstitials in the α-Zr lattice, are explicitly included in calculations. Precipitates are considered to be incoherent with the matrix, i.e. they can be considered as ideal sinks for point defects [9], and initially cubic in shape. The rate theory approach [8,15,16] is used to associate the micro and macro evolution of the crystal under irradiation.

2. Precipitation model

In Maydet and Russell's theory [14], precipitates are assumed to be spherical and considered as a binary substitutional solution dilute in solvent. They are characterized by two variables: x and n. The former is the

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Table 1
Material and irradiation parameters

Parameter	Value
K_i (production rate of interstitials)	3.00×10^{-8} dpa s^{-1} [20]
K_v (production rate of free vacancies)	2.97×10^{-8} dpa s^{-1} [20]
$\epsilon = K_v / K_i$	0.99 [20]
a_{zr} (lattice parameter α-Zr matrix)	0.323 nm [25]
a_{pr} (lattice parameter β-85 wt% Nb)	0.335 nm [25]
Ω_m (atomic volume of the hcp matrix)	23.26×10^{-3} nm^3
Ω (atomic volume of bcc precipitates)	18.80×10^{-3} nm^3
T (temperature)	560 K [20]
k (Boltzmann's constant)	0.862×10^{-4} eV K^{-1}
E (Young's modulus for Zr at 573 K)	
100 direction	466 eV nm^{-3} [29]
001 direction	613 eV nm^{-3} [29]
ν (Poisson's ratio for Zr at 573 K)	
100 direction	0.37 [29]
001 direction	0.48 [29]
γ (particle : matrix surface energy)	0.0312 eV (assumed)
$\langle D_v \rangle$ (fitted vacancy diffusivity)	1.4×10^{-21} m^2 s^{-1} [20]
E_v^f (vacancy formation energy)	1.8 eV [12]
c_v^e (equilibrium vacancy concentration)	$\exp(-E_v^f / kT)$
$S_v = c_v / c_v^e$ (vacancy supersaturation)	see table 2
c_x^e (solubility of Nb in α-Zr)	0.6 [27]
$S_x = c_x / c_x^e$ (impurity supersaturation)	1.67

number of solute atoms within the precipitate and the later is the number of excess vacancies in it, so that $(x + n)$ is equal to the number of matrix atoms displaced. The change rate in x or n, that moves the particle in the x or n directions, can be written as

$$\dot{x} = \beta_x(n, x) - \alpha_x(n, x), \quad (1)$$

$$\dot{n} = \beta_v(n, x) - \alpha_v(n, x) - \beta_i(n, x), \quad (2)$$

where β_x, β_v and β_i are the arrival rates of solutes, vacancies and interstitials to precipitate and α_x and α_v are the rates of loss of solute and vacancies, respectively. If α_x and α_v are replaced in eqs. (1) and (2) by their expressions as calculated in ref. [14], nodal lines can be obtained by setting eqs. (1) and (2) individually equal to zero.

For $\dot{n} = 0$

$$n = x\{\delta + (1/2B) \ln[S_v(1 - \beta_i/\beta_v)]\}, \quad (3)$$

and for $\dot{x} = 0$

$$n = x\delta\{1 + 2A/3B\delta^2 x^{1/3} - (1/B\delta^2) \ln S_x\}^{1/2}, \quad (4)$$

where

$$A = (36\pi\Omega^2)^{1/3}(\gamma/kT), \quad (5)$$

$$B = \Omega E/9kT(1 - \nu), \quad (6)$$

and

$$\delta = (\Omega - \Omega_m)/\Omega_m. \quad (7)$$

The meaning and values of symbols are summarized in tables 1 and 2.

If the nodal lines intersect at n^* and x^*, the point of intersection is known as the critical point. To this critical point corresponds the critical radius of the particle

$$r^* = -2\gamma\Omega/\Delta\Phi, \quad (8)$$

Table 2
Vacancy supersaturation S_v

Neutron fluence ($n\ m^{-2} \times 10^{24}$)	S_v ($\times 10^{12}$)
0.0	5.69
3.21	5.68
8.58	5.66
13.96	5.65
16.65	5.63
19.35	5.61
24.71	5.60
27.40	5.58
32.78	5.57

where $\Delta\Phi$ is an irradiation-modified potential [17] given by

$$\Delta\Phi = -kT\{\ln S_x[S_v(1-\beta_i/\beta_v)]^\delta + (1/4B)[\ln S_v(1-\beta_i/\beta_v)]^2\}. \quad (9)$$

Unlike Maydet and Russell's theory, initially cubic precipitates, considered to be incoherent with the matrix, are assumed in this work, as in ref. [13]. In this case, the corresponding critical size d^* of particles is [13]

$$d^* = -3.2\gamma\Omega/\Delta\Phi. \quad (10)$$

In general, precipitates with $d > d^*$ will grow, while if they have $d < d^*$, they are unstable and will decay. If $\Delta\Phi > 0$ the nodal lines do not intersect for $x > 0$ and all particles will decay.

3. Parameter evaluation

To analyze the stability of precipitates formed in the α-Zr (1 wt% Nb) matrix of the in-service nuclear reactor pressure tubes, the values of d^* for different strain states of the material must be calculated. Therefore, all parameters in $\Delta\Phi$ must be evaluated.

3.1. Vacancy supersaturation

The vacancy supersaturation is defined as

$$S_v = c_v/c_v^e, \quad (11)$$

where c_v^e is the thermal equilibrium vacancy concentration and c_v is the actual vacancy concentration, both in the matrix.

By assuming different production rates of free interstitials and vacancies (K_i and ϵK_i, where $\epsilon < 1$, respectively) [18,19], for the steady state case, c_v is [20]

$$c_v = (k_i^2\langle D_i\rangle/2\alpha)\{-(1-\xi') + [(1+\xi')^2+\Psi]^{1/2}\}, \quad (12)$$

where

$$\xi' = \xi + [\alpha K_i(\epsilon-1)]/k_v^2\langle D_v\rangle k_i^2\langle D_i\rangle, \quad (13)$$

$$\xi = \alpha c_v^e/k_i^2\langle D_i\rangle, \quad (14)$$

and

$$\Psi = 4\alpha K_i/k_v^2\langle D_v\rangle k_i^2\langle D_i\rangle. \quad (15)$$

$\langle D_v\rangle$ and $\langle D_i\rangle$ are the average vacancies and interstitials diffusivities and α is the mutual recombination constant. k_v^2 and k_i^2 are the total sink strengths for vacancies and interstitials considering all sinks present in the material, i.e dislocations, grain boundaries and precipitates.

For the high dislocation density case of cold-work materials, and from the behavior of the grain boundary and precipitate sink strengths versus dislocation density [11,13], the total sink strengths for vacancies and interstitials are approximately equal to the dislocation sink strengths for vacancies and interstitials, respectively [13]. An approximate expression for prismatic dislocation sink strengths as a function of the anisotropy (D_c/D_a), being D_c the diffusivity parallel to **c**-lattice axis and D_a the diffusivity perpendicular to **c**-lattice axis, can be obtained as follows (see fig. 3 in ref. [12]):

$$k_d^2 = [4.85 - 2.83(D_c/D_a) + 1.05(D_c/D_a)^2 - 0.13(D_c/D_a)^3] \times 10^{14}\ \mathrm{m}^{-2}, \quad (16)$$

where the numerical coefficients result from assuming a dislocation density of $7\times10^{14}\ \mathrm{m}^{-2}$ in the material. By replacing (D_c/D_a) by the corresponding values for vacancies and interstitials, the prismatic dislocation sink strengths for vacancies and interstitials may be calculated. Then, c_v and S_v can be obtained.

3.2. (β_i/β_v) ratio

As already mentioned, β_i and β_v are the arrival rates of interstitials and vacancies, produced by irradiation, from the matrix to the precipitate. From the anisotropy of the diffusion tensor in hcp materials, each face in the precipitate takes up different number of vacancies and different number of interstitials, according to its orientation with respect to the hcp crystal lattice, the so-called diffusional anisotropy difference (DAD) [16]. Therefore, the behavior of different faces will be taken into account explicitly in order to calculate β_i/β_v in $\Delta\Phi$. Henceforth, for simplicity in the analysis of results, the **c**-lattice and the **a**-lattice axes are taken to be parallel to the edges of the precipitate. If the latter condition is relaxed, the new corresponding β_i/β_v ratio over each face should be considered. The above assumption does not invalidate the incoherent character assumed for the matrix–precipitate interface.

From the definition of precipitate partial sink strengths (the sink strength of each precipitate face [13]), the ratio β_i/β_v for the face whose normal is parallel to **c**-lattice direction can be calculated as

$$(\beta_i/\beta_v)_c = (k_{c\,\mathrm{pri}}^2\langle D_i\rangle c_i)/(k_{c\,\mathrm{prv}}^2\langle D_v\rangle c_v), \quad (17)$$

where $k^2_{c\,\mathrm{pri,v}}$ are the partial precipitate sink strengths of the face whose normal is parallel to the $\boldsymbol{c}$-lattice direction, for interstitials and vacancies, respectively.

The precipitate partial sink strength of the face perpendicular to $\boldsymbol{c}$-axis, can be obtained as a function of the anisotropy factor (D_c/D_a) (see the appendix in ref. [13]). In particular, if a density of $9 \times 10^{19}\ \mathrm{m}^{-3}$ cubic precipitates of 0.03×10^{-6} m in size is assumed, $k^2_{c\,\mathrm{pr}}$ can be approximated by

$$k^2_{c\,\mathrm{pr}} = \left[0.62(D_c/D_a) + 0.41\right] \times 10^9\ \mathrm{m}^{-2} \tag{18}$$

in the $(D_c/D_a) = 0.7 - (D_c/D_a) = 0.8$ range, and by

$$k^2_{c\,\mathrm{pr}} = \left[0.19(D_c/D_a) + 0.83\right] \times 10^9\ \mathrm{m}^{-2} \tag{19}$$

in the $(D_c/D_a) = 1.8 - (D_c/D_a) = 2.0$ range. The choice of these particular ranges and the geometry of precipitates will be justified in section 5. If $(D_c/D_a)_\mathrm{i}$ or $(D_c/D_a)_\mathrm{v}$ values (i (v) indicates interstitial (vacancy)) replace to (D_c/D_a) in eq. (18) or eq. (19), the corresponding partial sink strength for interstitials or vacancies may be obtained in the mentioned ranges.

For the same conditions as 3.1, c_i, the actual interstitials concentration, is [20]

$$c_\mathrm{i} = \left(k^2_\mathrm{v}\langle D_\mathrm{v}\rangle/2\alpha\right)\left\{-(1+\xi) + \left[(1+\xi')^2 + \Psi\right]^{1/2}\right\} - \left[K_\mathrm{i}(\epsilon - 1)/2k^2_\mathrm{i}\langle D_\mathrm{i}\rangle\right]. \tag{20}$$

The value of $\langle D_\mathrm{v}\rangle$ is used as a variable parameter to fit the experimental result of the axial change of shape of a pressure tube in-service [20,21]. Finally, if the expression by the recombination constant in hcp materials given by Fainstein-Pedraza et al. ($\alpha = 21\langle D_\mathrm{i}\rangle/a^2$, where a is the lattice parameter) [22,23] is introduced, eq. (17) does not depend on $\langle D_\mathrm{i}\rangle$.

Similarly $(\beta_\mathrm{i}/\beta_\mathrm{v})_a$, the ratio for the faces whose normals are perpendicular to the $\boldsymbol{c}$-lattice direction, can be calculated as

$$(\beta_\mathrm{i}/\beta_\mathrm{v})_a = \left(k^2_{a\,\mathrm{pri}}\langle D_\mathrm{i}\rangle c_\mathrm{i}\right)/\left(k^2_{a\,\mathrm{prv}}\langle D_\mathrm{v}\rangle c_\mathrm{v}\right), \tag{21}$$

where $k^2_{a\,\mathrm{pri,v}}$ are the partial precipitate sink strengths of the corresponding faces, for interstitials and vacancies, respectively.

4. Evolution of the diffusion anisotropy in pressure tubes

In hexagonal strained materials, the diffusion anisotropy (D_c/D_a) of vacancies and interstitials depends on the intrinsic anisotropy of the lattice and on the elastic strain generated by external and internal stresses. The effect of the induced strain field $(\boldsymbol{\Gamma})$ on the defect diffusivity can be obtained explicitly as [4,5]

$$D^\Gamma_{ij} = d_{ijkl}\Gamma_{kl}, \tag{22}$$

where $\boldsymbol{d}$ is the elastodiffusion tensor for vacancies or interstitials. Therefore, the total diffusivity tensor $\boldsymbol{D}$ results:

$$D_{ij} = D^\circ_{ij} + d_{ijkl}\Gamma_{kl}, \tag{23}$$

where $\boldsymbol{D}^\circ$ is the point defect diffusion tensor in the strain free crystal. In most cases, the tetragonal symmetry is lost and both diagonal basal components (D_{11} and D_{22}) of $\boldsymbol{D}$ are different. But in the present work they are close enough, therefore the anisotropy of the diffusion will be approximated by D_c/D'_a where $D'_a = (D_{11} + D_{22})/2$ and $D_c = D_{33}$. This anisotropy of the diffusion as a function of the evolution of the internal stresses developed in a pressure tube in-service, in turn a function of the microstructure, grain orientations, irradiation and time, is obtained from a modified code [20]. The latter is based on the model proposed by Savino and Laciana [2], to calculate the macroscopic change of shape of an irradiated pressure tube under an external below-yield-stress field and the induced intergranular stresses. In the modified code [20], the developed explicit expressions for the vacancy and interstitial elastodiffusivity tensors in a strained hcp lattice, as a function of the defect equilibrium and saddle-point dipole tensors [5], are introduced. Then, $d_{ijkl}\Gamma_{kl}$ for each defect can be calculated. From (23), and calculating previously D°_{ij} for vacancies and interstitials, $D_{c_{\mathrm{v,i}}}$, $D'_{a_{\mathrm{v,i}}}$ and $(D_c/D'_a)_\mathrm{v,i}$ are obtained.

Previous results in ref. [11], that allow the expression of the grain boundary sink strengths as a function of the anisotropy, eqs. (16), (18) and (19), and the texture and microstructure of the pressure tube, described in the next section, are also introduced in the code.

A temperature jump of 260 K from a state free of internal stresses, is imposed as initial condition in the calculations.

Point defects in each grain are treated within the rate theory approach for anisotropic materials [16].

5. Application to cold-work pressure tubes of Zr–2.5 wt% Nb

Maydet and Russell's theory [14] is applied in this section to analyze the experimentally observed precipitation of the β-85 wt% Nb phase in the α-Zr (1 wt% Nb) matrix of pressure tubes of CANDU reactors [24].

Some of the irradiation and material parameters used are given in table 1. To calculate $\Delta\Phi$, except for S_x, the hcp α-Zr (1 wt% Nb) is assumed to be α-Zr pure phase. This phase is described by a strongly repulsive potential adjusted to a vacancy formation energy of 1.8 eV [12]. Assuming the vacancy migration energies 1.440 eV and 1.500 eV for the nonbasal and basal jump [12] respectively, the vacancy anisotropy factor $(D_c/D_a)_v$ in the unstrained material at 560 K is 2.14 [13]. Also, if the interstitial equilibrium configurations are taken as the basal octahedral (formation energy: 4.547 eV) and the trigonal (formation energy 4.701 eV) configurations [12], and the interstitial saddle-point configuration is taken as the dumbbell configuration for both equilibrium configurations (migration energy 4.831 eV) [12], the interstitial anisotropy factor $(D_c/D_a)_i$ is 0.60 [13] for the same material conditions. These anisotropies of the diffusivity change in the presence of external stresses and when intergranular stresses begin to develop.

The microstructure of cold-work Zr–2.5 wt% Nb pressure tubes consists of two phases: hcp parallelepiped α-grains containing about 1 wt% Nb and a homogeneous dislocation density of about 7×10^{14} m^{-2}, and a bcc β-phase containing about 20 wt% Nb at the α-grain boundaries [25,26]. This density of dislocations, assumed to be prismatic edge dislocations, and the grain boundaries of the parallelepiped shaped α-grains (35×10^{-6} m in the axial direction (A), 7×10^{-6} m in the tangential direction (Tg) and 0.7×10^{-6} m in the radial direction (R)) are considered as point defect

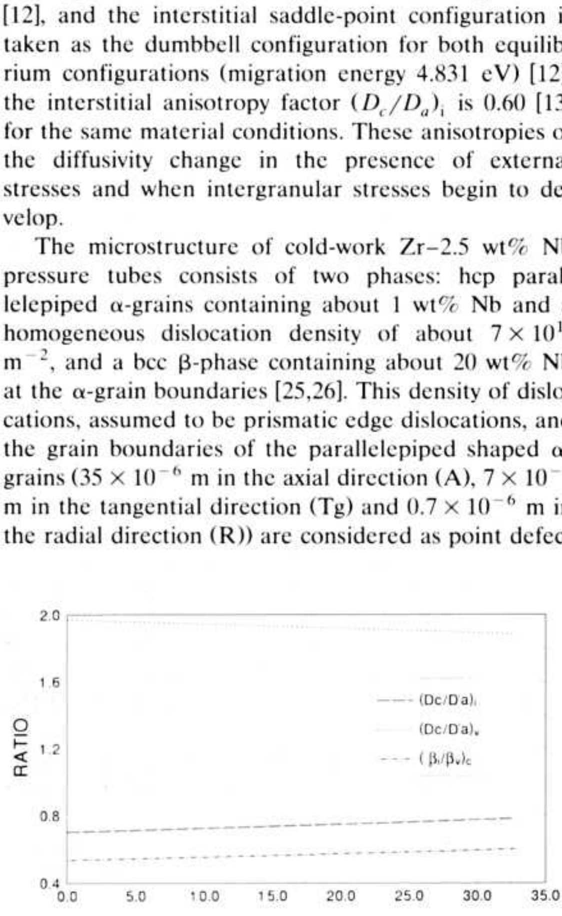

Fig. 1. Anisotropy of the diffusion of vacancies $(D_c/D'_a)_v$ and interstitials $(D_c/D'_a)_i$ in the hcp α-Zr matrix of the in-service pressure tubes and arrival rates ratio $(\beta_i/\beta_v)_c$, as a function of the neutron fluence at $T = 560$ K. β_i (β_v) is the arrival rate of interstitials (vacancies) from the matrix to the faces of bcc β-85 wt% Nb precipitates perpendicular to **c**-lattice axis. D_c is the diffusivity parallel to **c**-lattice axis and D'_a the average basal diffusivity.

sinks and thermal sources of vacancies in the modified code. Also, a homogeneous cubic precipitate (0.03×10^{-6} m in size) density $\rho_{pr} = 9 \times 10^{19}$ m^{-3} within the α-Zr matrix is assumed as a sink of point defects and a source of vacancies [13].

The concentration of Nb in the α-Zr matrix is considered to be equal to the value of the unstrained material: 1 wt%. Assuming the phase diagram [27] to be also valid, $S_x = 1.67$.

From ref. [28], the texture of the pressure tube is represented by three different grain orientations [21]: **c** on R–Tg plane, $\pm 80°$ from R axis (volume density 0.6); **c** on R–Tg plane, $\pm 70°$ from R axis (0.2); **c** on R–Tg plane, $\pm 90°$ from R axis (0.2). Henceforth, for simplicity, only analyses on grains with this last orientation shall be considered. The behavior of precipitates within grains with other orientations will be similar, because of the small disorientation between grains.

The external stress (hoop stress) is taken as 136 MPa [29].

The evolution of $(D_c/D'_a)_{v,i}$ with the neutron fluence, calculated as described in section 4, is shown in fig. 1. From these results and from eq. (16), the values of k_d^2 are calculated for vacancies and interstitials, and they are introduced in eqs. (12) and (20) to obtain c_v and c_i. The corresponding values for vacancy supersaturations at 560 K, as calculated by assuming $1 - \epsilon = 1\%$, are presented in table 2. Also, from the $(D_c/D'_a)_{v,i}$ evolution, from eqs. (18), (19) and (17), $(\beta_i/\beta_v)_c$ is obtained as a function of the neutron fluence (fig. 1).

From fig. 1 it can be seen that $(D_c/D'_a) > 1$ for vacancies, $(D_c/D'_a) < 1$ for interstitials and $(\beta_i/\beta_v)_c < 1$ at the neutron fluences considered. Furthermore, from the same figure and from the behavior of $k_{a\,pr}^2$ versus (D_c/D_a) (see fig. 4 in ref. [13]), it results $k_{a\,pri}^2 > k_{a\,prv}^2$ and, consequently, is $(\beta_i/\beta_v)_a > 1$.

As the (β_i/β_v) ratio is smaller than one for precipitate faces perpendicular to the **c**-lattice direction, and greater than one for precipitate faces parallel to the **c**-lattice direction, the behavior of each face is taken into account explicitly in order to calculate $\Delta\Phi$.

5.1. $(\beta_i/\beta_v) < 1$ (faces of the precipitate perpendicular to the c-lattice direction)

Fig. 2 shows the values d^*/a_{pr} at 560 K, where d^* is measured in the perpendicular direction to the face being considered, for different neutron fluences. These values are obtained from parameters described in tables 1 and 2, introduced in eq. (9) and then in eq. (10). B values are calculated taking $E(100)$ and $\nu = [\nu(100) + \nu(001)]/2$ because the growth in the **c**-direction is analyzed. Ω and Ω_m are considered to be the same as the corresponding values in the unstrained matrix.

All particles of β-85 wt% Nb present in the material with $d > d^*$ will be able to grow.

*5.2. $(\beta_i/\beta_v) > 1$ (faces of the precipitate parallel to the **c**-lattice direction)*

The nodal line $\dot{x} = 0$ at 560 K is shown in fig. 3.

For faces with $(\beta_i/\beta_v) > 1$, it is not possible to define a priori the nodal line $\dot{n} = 0$ (see eq. 2), and consequently it is not possible to defined d^*. However, as it was analyzed in ref. [13], as the interstitial sites in the bcc structure are smaller than $0.25r$, where r is in this case the Nb atomic radius, the irradiation-induced Zr self-interstitials would not occupy those sites. Then, once $n = 0$ inside the precipitate, only a number β_i' of these self-interstitials, equal to $(\beta_v - \alpha_v)$ could jump into the precipitate. Then, from eq. (2) it may be assumed that, in this case

$$\dot{n} \equiv 0. \tag{24}$$

The difference between β_i and β_i' may be accommodated in the incoherent precipitate–matrix interphase [8,9].

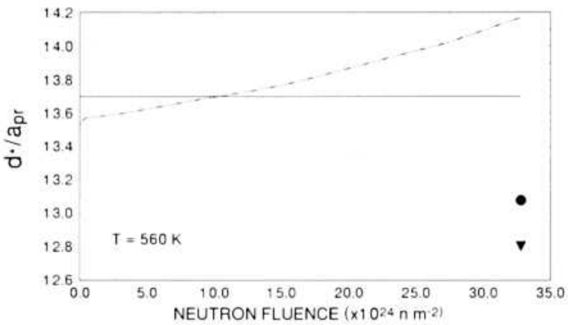

Fig. 2. Critical size ratio d^*/a_{pr} in the **c**-lattice direction for the precipitation of bcc β-85 wt% Nb in the anisotropic hcp α-Zr matrix of the in-service pressure tubes, at $T = 560$ K, as a function of the neutron fluence. Calculations were done by assuming that: (a) the pressure tube texture is represented by three grain orientations: **c**-lattice axis on the radial-tangential plane, $\pm 80°$, $\pm 70°$ and $\pm 90°$ from the radial-tube direction (· · · – · · ·). (b) the external hoop stress is released after the neutron fluence of 32.8×10^{24} n m^{-2}. Pressure tube texture represented by the latter three orientations (●). (c) the pressure tube texture is represented by one grain orientation: **c**-lattice axis parallel to the tangential-tube direction (———). (d) the external hoop stress is released after the neutron fluence of 32.8×10^{24} n m^{-2}. Pressure tube texture represented by the latter orientation (▼). a_{pr} is the lattice parameter of precipitates.

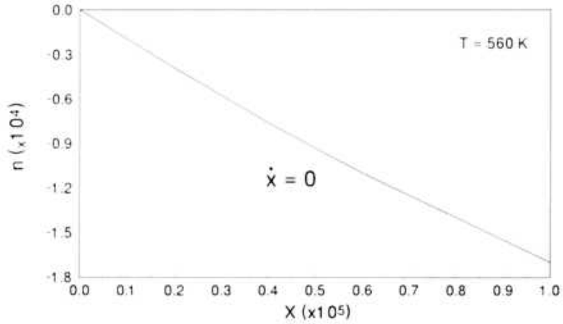

Fig. 3. Nodal line $\dot{x} = 0$ for the precipitation of β-85 wt% Nb in the α-Zr matrix of the in-service pressure tube, when faces parallel to **c**-lattice axis are considered. x is the number of solute atoms and n is the number of excess vacancies, both within the precipitate.

At temperatures lower than 600 K, the rate of emission of vacancies is negligible [13] and then, $\beta_i' = \beta_v$.

From eq. (24), from the condition

$$n = 0, \tag{25}$$

and from fig. 3 ($x = 0$ for $n = 0$), it follows that $d^* = 0$. Therefore, in directions perpendicular to **c**-crystal axis all particles will be able to grow, independently of their initial size.

6. Effect of intergranular and external stresses

The effect of intergranular stresses on d^* may be visualized by comparing the above values of d^*, obtained considering the texture mentioned in section 5 (texture of pressure tube), with the values of d^* obtained by assuming that all grains, in the pressure tube, have the **c**-lattice axis parallel to the Tg-tube direction. In this case, internal stresses are not developed and the anisotropies (D_c/D_a') for vacancies and interstitials will not change with the fluence. The calculated values are: $(D_c/D_a')_v = 1.95$ and $(D_c/D_a')_i = 0.72$, respectively. Consequently, its result: $(\beta_i/\beta_v)_c = 0.55$, $S_v = 5.66 \times 10^{12}$ and $d^*/a_{pr} = 13.7$. Fig. 2 shows that the latter value agrees with the d^*/a_{pr} value obtained in the textured polycrystal (texture of pressure tube), for the intermediate neutron fluence 10^{25} n m^{-2}. Then, it can be seen that intergranular stresses enhance the formation of the β-85 wt% Nb precipitates for neutron fluences lower than 10^{25} n m^{-2}, and hind their formation for neutron fluences greater than the latter one.

Table 3
$(D_c/D_a)_{i,v}$, $(\beta_i/\beta_v)_c$ and S_v for zero external stress

	Texture of pressure tube	$c \parallel$Tg-direction
$(D_c/D_a)_i$	0.63	0.60
$(D_c/D_a)_v$	2.09	2.14
$(\beta_i/\beta_v)_c$	0.48	0.42
S_v	5.82×10^{12}	5.86×10^{12}

If the external hoop stress is taken equal zero after 1.36×10^8 s (full power days 1576; neutron fluence 32.8×10^{24} n m^{-2}), $(D_c/D'_a)_i$, $(D_c/D'_a)_v$, $(\beta_i/\beta_v)_c$, and S_v take the values indicated in table 3 for both textures considered. Also, both d^*/a_{pr} calculated values are shown in fig. 2.

Finally, in the case of non irradiation (in this case $\Delta\Phi = -kT \ln S_x$ [10]) results $(d^*/a_{pr})_{NI} = 22.4$ at 560 K. This is the greater value obtained in the present work. However, as the impurity saturation S_x is obtained from a phase diagram of an unstrained material (see section 5), the latter value could be only compared with the value obtained when all grains have the c-axis parallel to the Tg-direction and the external stress is zero (see fig. 2 (▼)).

7. Discussion and conclusions

Critical sizes d^*, for bcc β-85 wt% Nb precipitates in the hcp α-Zr (1 wt% Nb) matrix of the in-service CANDU reactor pressure tubes, are calculated at 560 K in this paper. Precipitates are assumed to be initially cube-shaped and their precipitate–matrix interfaces incoherent.

Pressure tubes are considered to be formed by elongated α-Zr grains and their texture is assumed to be represented by three different orientations. An external hoop stress, and internal stresses generated from the individual grain distortions by irradiation growth and creep, are explicitly included in the calculation.

The anisotropic diffusion of vacancies and interstitials in the strained α-Zr phase of pressure tubes, is responsible of the different trapping of vacancies and interstitials in differently oriented precipitate faces. On account of this different trapping, $\Delta\Phi$ (eq. (9)) is calculated assuming first the corresponding (β_i/β_v) values for the face with its normal parallel to c-lattice axis ($(\beta_i/\beta_v)_c < 1$), and then for the faces with normals perpendicular to the c-lattice axis ($(\beta_i/\beta_v)_a > 1$). This behavior of the arrival rates ratio (β_i/β_v) agrees with the obtained in the unstrained α-Zr matrix [13], i.e. the latter behavior is not changed by external and internal stresses.

For the $(\beta_i/\beta_v)_c < 1$ case, and from the parameters calculated for different neutron fluences, $\Delta\Phi$ results negative and the particles will be able to grow in the c-direction if they have $d > d^*$. For the other directions, where the faces have their normals perpendicular to the c-crystal axis ($(\beta_i/\beta_v)_a > 1$), all particles will be able to grow, because $d^* = 0$. These results and the values of d^* from fig. 2 should indicate that precipitates of β-85 wt% Nb, formed in the α-Zr matrix of the in-service pressure tubes, have only a slightly anisotropic shape, with the smaller size in the c-crystal direction.

From fig. 2, it can be seen that the external hoop stress does not help the precipitation of the β-85 wt% Nb phase in the pressure tubes. In fact, when after 1.36×10^8 s (neutron fluence 32.8×10^{24} n m^{-2}) the hoop stress is released, d^*/a_{pr} decreases. Also, if it is assumed that all grains have the same orientation, d^*/a_{pr} increases from 12.8, when the hoop stress is zero, to 13.7 (see section 6) when the hoop stress is 136 MPa.

The effect of internal stresses depends on the neutron fluence (fig. 2). At neutron fluences lower than 10^{25} n m^{-2}, the internal stresses developed from the texture of pressure tubes help the formation of the β-85 wt% Nb precipitates in these tubes; this behavior is reversed for higher neutron fluences.

Finally, by comparing the d^*/a_{pr} obtained values with the corresponding one for the case of nonirradiation: $(d^*/a_{pr})_{NI} = 22.4$ (section 6), we can see that the formation of β-85 wt% Nb precipitates in pressure tubes of CANDU reactors should be enhanced by irradiation at 560 K.

The enhanced precipitation and the predicted morphology agree with the experimental observed ones, according to Griffitts [24].

The results obtained for the stability and shape of the β-85 wt% Nb precipitates formed in the hexagonal α-Zr matrix of the in-service CANDU reactor pressure tubes, are a direct consequence of explicitly including in the calculations the evolution of the anisotropy of the diffusion of vacancies and interstitials with the neutron fluence. This anisotropy results from the intrinsic anisotropy of the lattice and from an additional one, introduced by internal stresses generated from external stresses, the microstructure and the texture of the pressure tubes.

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