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Updated Model for Predicting Spent Fuel Cladding Integrity During Dry Storage

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FINAL DRAFT REPORT

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ABSTRACT

This report presents a method for assessing the level of damage that Zircaloy cladding will sustain over the life of a spent-fuel dry-storage installation. This method substantially updates the original diffusion-controlled cavity growth (DCCG) model proposed by LLNL in the mid 1980s. The purposes of this update are to provide both an improved thermal-physical basis for modeling DCCG and, in the process, improve the material-dependent properties required as input to the model. This updated model is compared to the original model and recommendations for further model development and investigations of Zircaloy material and irradiation properties are made.

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NOMENCLATURE (In order of presentation)

DCCG	Diffusion-controlled cavity growth.					
r	Radius of curvature for a cavity (m).					
r _c	Critical radius of curvature for the initially stable nuclear cavity (m).					
Гb	Grain boundary planar radius of a growing cavity (m).					
r _{bc}	Grain boundary planar radius of the nuclear cavity (m).					
α	Intersection angle between the cavity spherical surface and the grain boundary.					
Es	The surface energy of the material (J/m^2) .					
γ	The surface tension of the material (N/m or J/m ²).					
γ _b	Grain boundary interface force of the material (N/m or J/m ²).					
σn	Normal stress across the grain boundary (N/m ²).					
λ	Cavity separation distance, centerline-to-centerline, on a planar surface representing contiguous grains (m).					
Α	Square of the ratio of r_b to $\lambda/2$ as a measure of damage to (separation of or decohesion of) a planar surface representing contiguous grains caused by cavities.					
Ai	The function A evaluated at $r = r_c$ defining the measure of initial decohesion of a given grain boundary surface as a result of the nuclear cavities.					
λ_i	Initial cavity spacing associated with A _i (m).					
P _N	Probability of forming a stable nuclear cavity.					
∆G*	Minimal free energy of a stable nuclear cavity (J).					
k	Boltzmann's constant (1.3806 J/K).					
Т	Absolute temperature (K).					
Sv	Surface area of the cavity (m ²).					
Sb	Planar surface area of a grain boundary displaced by a cavity (m^2) .					
$\mathbf{V}_{\mathbf{v}}$	Volume of the cavity nucleus (m ³).					
Dgb	Vacancy diffusion coefficient within the grain boundary, i.e., applies within the grain boundary plane thickness δ (m ² /sec).					
D _v	Bulk grain self-diffusion or vacancy diffusion coefficient within the grain boundary (m ² /sec).					

- A_o Grain boundary surface area per stable nuclear cavity (m²).
- C_{VA} Grain boundary surface vacancy density (Vac/m²).
- Ω Atomic volume of the material (m³).
- ρ Density of the material (kg/m³).
- A_v Avogadro's number (6.02 x 10²⁶ atoms/kg-mole).
- M Molecular weight of the material (kg/kg-mole).
- N_v Vacancy density in the matrix (vacancy/atom).
- N_o Base value for vacancy density in the matrix (vacancy/atom).
- K Material-dependent parameter defined in Eq. 31.
- F_B Displaced grain boundary area function defined in Eq. 35.
- F_V Cavity volume function defined in Eq. 36.
- δ Grain boundary plane thickness which is typically taken as about 10 nm or less (m).
- P Grain boundary diffusion parameter which is equivalent to the product δD_{gb} (m³/sec).
- D General form for the temperature-dependent diffusion coefficient (m²/sec); subscripts v and gb refer to volume (bulk) and grain boundary processes respectively.
- D_o General form for the base (pre-exponential) diffusion coefficient (m²/sec); subscripts v and gb refer to volume (bulk) and grain boundary processes respectively.
- QD General form for the activation energy for the diffusion process (kJ/kg-mole); subscripts v and gb replacing D refer to volume (bulk) and grain boundary processes respectively.
- R Universal gas constant (8.3143 kJ/kg-mole-K).
- h_{fv} Volumetric heat of fusion of the material (J/m³).
- E Young's modulus (N/m²).
- b Burgers vector taken as 3.2323 Å from the zirconium value.
- D_{veff} Effective bulk grain self-diffusion or vacancy diffusion coefficient within the grain boundary enhanced by dislocation diffusion (m²/sec).
- Dgbeff Effective vacancy diffusion coefficient within the grain boundary enhanced by dislocation diffusion (m²/sec).
- δD_{gbeff} Effective vacancy diffusion parameter within the grain boundary, i.e., applies within the grain boundary plane thickness δ (m³/sec).
- Peff Grain boundary diffusion parameter which is equivalent to the 200v and duct δDgbeff (m³/sec).
- QP Activation energy for the effective grain boundary diffusion parameter (kJ/kg-mole).

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d Distance characteristic of the grain volume associated with the vacancies available for initial cavity nucleation at the grain boundary which is assumed to be equal to twice the height of the spherical cavity segment (m)

HCP "Hexagonal-close packed" in reference to the α -zirconium crystal structure.

Å Angstroms (1*10⁻¹⁰ m).

nm nanometers $(1*10^{-9} \text{ m}) = 10 \text{ Å}$.

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Updated Model for Predicting Spent Fuel Cladding Integrity During Dry Storage

1. Introduction

This report describes an updated version of a model, originally developed by the Lawrence Livermore National Laboratory (LLNL), for predicting possible lifetime limiting conditions of spent nuclear fuel rods during long-term dry storage.¹ This report is divided into four sections:

- Section 1 briefly covers some of the background of modeling this phenomenon, including short discussions of other modeling approaches
- Section 2 presents the updated LLNL model
- Section 3 compares this updated model to the original model and limited data
- Section 4 provides conclusions and recommendations

1.1 Background

In the mid 1980s, LLNL developed a methodology for predicting possible lifetime limiting conditions that could lead to gross failure (gross breaching of the cladding) of spent nuclear fuel rods during long-term dry storage.¹ This methodology was adopted by the Nuclear Regulatory Commission (NRC) ^{2,3} as a basis for establishing peak temperature limits during the dry storage period.

Long-term dry storage. In this context, long-term dry storage of spent nuclear fuel rods refers to the use of gas-inerted casks for storing intact nuclear fuel assemblies that have completed both reactor irradiation and several years of post-irradiation storage in spent fuel storage pools. The dry storage is expected to last for a few to several decades. The LLNL methodology was based on a slowly occurring, creep-induced failure mechanism known as diffusion-controlled cavity growth (DCCG)—a phenomenon which has been well established and described in the open literature for several decades.⁴⁻⁷

The DCCG process. The basic process involved in DCCG is the formation and growth of small cavities (voids) on the grain boundaries of a metal subjected to both reasonably high temperatures and a sustained stress loading. Growth of the cavities is believed to arise primarily from the diffusion of vacancies, formed originally within the matrix of the metal grain, to the

cavities. It is believed that the primary vacancy pathway involves diffusion to the grain boundaries (and hence along the grain boundaries, where diffusion is more rapid), to the cavities. As the cavities grow, the cohesion between adjoining grains proportionally decreases until intergranular failure can occur.

The concern regarding lifetime limiting conditions for spent nuclear fuel rods is that local dry storage conditions could be sufficiently severe and sustained that local pockets of DCCG-damaged spent fuel rods could form and grow cavities that eventually result in sudden and extensive failures.

Direct evidence that Zircaloy-2 and Zircaloy-4 were susceptible to DCCG is sparse.^{8,9} These zirconium-based alloys are the most commonly used nuclear fuel rod cladding materials with Zircaloy-2 predominant in boiling water reactors (BWRs) and Zircaloy-4 predominant in pressurized water reactors (PWRs). The alloys are composed of about 98+% zirconium and small percentages of Sn (1.2-1.7%), Fe (0.07-0.24%), Cr (0.05-0.15%) and Ni (0.03-0.08%), with the latter in Zircaloy-2 only.¹⁰ Furthermore, the specific evidence presented in References 8 and 9 has come into question regarding direct applicability to dry storage conditions.¹¹ (The Zircaloy data in References 8 and 9 were reviewed by the authors of Reference 11. They concluded that the testing conditions utilized in References 8 and 9 were stress-corrosion-cracking conditions, and that the resulting locations identified as cavities were, instead, corrosion pitting. An independent review by one of the authors of Reference 11 resulted in the same conclusion.) However, the DCCG process has been verified for some metals and alloys at conditions similar to the temperatures and stress conditions seen in spent fuel dry storage environments.^{12,13}

Since the original spent fuel storage DCCG model was developed, much new information has become available regarding physical properties, conditions, and parameters that govern general creep behavior and self-diffusion processes for pure α -phase zirconium and, to a limited degree, Zircaloy. The α -phase is the stable form for all zirconium contained in Zircaloy at all temperatures consistent with normal nuclear reactor operation and spent fuel storage conditions.

The original Zircaloy DCCG modeling¹⁻³ involved several assumptions and simplifications that were necessary based on the state-of-the-art knowledge of zirconium and Zircaloy behavior at that time. Now, updated Zircaloy DCCG modeling methods are essential because, over time, we have developed an increased understanding of applicable thermal physics and a more extensive data base of zirconium and Zircaloy creep and deformation behavior.

Note: the vast majority of new information relevant to improving Zircaloy DCCG modeling comes from the study of essentially pure α -phase zirconium. In many cases, the data are from

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experiments on single crystal grains of α -phase zirconium. Some of the very fundamental aspects of Zircaloy DCCG behavior must be considered in light of how both the more complex microstructure of the actual Zircaloy alloys and the added crystal lattice damage caused by irradiation could affect such behavior.

1.2 Other approaches for defining spent fuel lifetimes

The nuclear industry, in conjunction with the Department of Energy (DOE), has developed a different, but still creep-based, model for predicting lifetime limiting conditions of spent nuclear fuel rods. This model¹⁴ uses constitutive equations describing Zircaloy creep behavior originally developed by Chin.¹⁵ In an appendix to Reference 14, this model was compared to the original LLNL DCCG model—the results indicated that there was no significant difference in predicted lifetimes between the two models for identical storage conditions.

A recent study sponsored by the Electric Power Research Institute (EPRI) titled "Temperature Limit Determination for the Inert Dry Storage of Spent Nuclear Fuel"¹¹ has summarized much of the existing data base on experimentally determined failure modes from internally pressurized prototypical Zircaloy cladding sections, which are the most appropriate specimens for direct application to dry storage conditions.

These experimental tests involve both unirradiated and irradiated Zircaloy cladding with the latter being obtained from actual irradiated fuel rods. All of the reported tests (299 total) fall within the temperature range typically associated with peak dry storage conditions (a testing range of 292-400°C). However, less than one-tenth of the tests fall within the upper limit of peak dry storage stress conditions assumed in the original study of nearly 200 MPa.¹; and only two tests are equal to or less than a stress level of 130 MPa. (The EPRI report makes a reasonable argument that a conservative peak stress for spent fuel storage conditions should be less than about 130 MPa.) As an added complexity in using these test data, the majority of the tests (256) involved varying stress-corrosion-cracking conditions. The applicability of these SCC tests have to be considered carefully in applying them to the DCCG arena.

In addition, the EPRI report summarized current German and Japanese nuclear industry approaches for predicting lifetime limiting conditions of spent nuclear fuel rods. In both instances, the approach basically involves limiting permitted permanent spent nuclear fuel rod cladding strains to 1%, as characterized by the experimentally determined creep behavior of Zircaloy discussed in the report and modeled by Romeiser and Steinberg¹⁶ and Mayuzmi and Onchi.^{17,18}

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In the case of the German approach,¹⁶ conservatism is added by considering the creep behavior of more-ductile unirradiated Zircaloy cladding as a basis for setting the permitted dry storage limits for the less-ductile (higher effective creep strength) irradiation-hardened Zircaloy cladding of spent nuclear fuel rods. However, the authors of the EPRI report cautioned that the German creep data base is based on Zircaloy fabricated in Germany; and before such an approach could be considered in the United States, the creep behavior of US-produced Zircaloy needs comparable characterization.

2. Updated DCCG modeling

2.1 DCCG model

Since the late 1950s⁴, the possibility of creep-caused formation of cavities at grain boundaries has been identified as a slowly developing mode of material failure that can occur at relatively low stress levels and relatively high temperatures. The progressive growth of the cavities in this situation is believed to be caused by diffusion of vacancies.

A notable and continuous source of these vacancies, which can be precisely defined, is the spontaneous creation of vacancies from simple thermal driving forces within the matrix of the grains. Other possible sources of these vacancies can result from distortions of the grain matrix caused by such phenomena as a more complex and continuous source from intra-grain matrix effects of both temperature and stress; and, as primarily initial sources (at the start of dry storage conditions) of vacancies and cavities:

- (1) presence of foreign (alloying) atoms
- (2) metal fabrication and/or work-hardening processes
- (3) irradiation damage (potentially the most significant source for Zircaloy).

In this context, initial refers to conditions present at the start of dry storage. In addition, these same sources can contribute to an increase in the initial cavity density (cavities per unit area) at grain boundaries.

Regardless of the source, once these vacancies are formed in the matrix of the grains, they can thermally diffuse to the grain boundaries (acting as vacancy sinks). Once at the grain boundaries, the vacancies can move with less resistance (more rapidly) along the grain boundaries and, under applied stress-temperature conditions, can move preferentially to cavity nucleation sites. At a minimum, the sites of these nuclear cavities can be small and stable cavities that are initially formed spontaneously on grain boundaries. The cavities would be formed by a balance between the addition of vacancies by thermal diffusion (primarily along the grain boundaries) and the subtraction of vacancies by thermal diffusion back into both the grain boundaries and the grain matrix. In addition, the cavities can initiate at inclusions (e.g., at clusters of alloying atoms) in the grain boundaries, at grain boundary junctions, or at grain boundary defects, caused, for example, from some of the effects noted in the previous paragraph.

With an upset in the stress-temperature conditions, these cavities can either grow or shrink. If there is an increase in the severity of the stress-temperature conditions, then these cavities can grow—a process that has been labeled as diffusional growth of cavities¹⁴⁻¹⁵ or, as used in this report, diffusion-controlled cavity growth.¹ It is this latter term, or DCCG, that will be used throughout this report to represent the cavity growth process.

As described above, the DCCG process is essentially the result of the progressive movement of vacancies from the grain matrix to grain boundaries, and then along grain boundaries to one of many naturally occurring cavities located on the grain boundaries which are initially in equilibrium as nuclear cavities. Each equilibrium or nuclear cavity has a critical radius of curvature, r_c , that is a simple free-energy and force-balance function of a material property:

$$\mathbf{r}_{\epsilon} = 2 \frac{\gamma}{\sigma_{\mathrm{n}}},\tag{1}$$

where

 γ (which is effectively identical to the surface energy, E_s) is the surface tension and

 σ_n is the stress normal to the grain boundary.

As treated previously¹⁻⁶ and in this report, it is assumed that there is no pressure in the cavities.

To describe this process, an individual nuclear cavity geometry at a cavity nucleation site is assumed to consist of mirror-image spherical surface segments symmetrical about the grain boundary (Figure 2.1); and that the cavity nucleation sites retain their spherical surface segment shape as they grow beyond the critical size through a net collection of vacancies.^{1,5,6} It is also assumed that the cavities are arrayed on a given surface of a grain of a material in a regular pattern separated, centerline-to-centerline, by an average distance, λ , as shown in Figure 2.2 (in this figure, the viewer is looking down on the plane surface of a grain boundary).

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Figure 2.1 Diffusit a mean clear cavity growth geometry (two mirror-image spherical cavity segments symmetrical about the grain boundary)

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Because of the spherical surface shape assumption, which is consistent with both a force balance on the cavity and a minimizing of free surface energy, it is possible to define both the intersection angle between a cavity spherical surface and the grain boundary plane, α , and the grain boundary planar radius of a growing cavity, $r_b(t)$. The former requires the introduction of another material property, the grain boundary interface force, γ_b . From the enlarged view of the cavity-grain boundary shown in Figure 2.1, it can be seen that the component of the cavity surface tension parallel to the grain boundary, or $\gamma \cos \alpha$, opposes the grain boundary interface force, γ_b . Because there are two sides of the cavity in balance (two adjacent spherical segments in two adjacent grains),

$$2\gamma\cos\alpha = \gamma_0 \tag{2}$$

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$$\cos\alpha = \frac{\gamma_{e}}{2\gamma}.$$
 (3)

From the spherical surface characteristics, the grain boundary planar radius of a growing cavity, $r_b(t)$, can be related to the cavity radius of curvature

$$r_{\rm h} = r \sin \alpha$$
 (4)

If Eq. 4 is evaluated at $r = r_c$, then the critical grain boundary planar radius of the nuclear cavity, r_{bc} , can be found.

A time-dependent function A(t) is commonly used to relate cavity size to gross damage to (separation of or decohesion of) a given grain boundary surface. Considering a cavity spacing of λ , if the cavity radii reach a value of $\lambda/2$ there would be a continuous or 100% linear decohesion of the grain boundary surface. The function A(t) is the square of the ratio of $r_b(t)$ to $\lambda/2$:

$$A(t) = \left(\frac{r_{b}(t)}{\lambda_{2}}\right)^{2} = \left(\frac{r(t)\sin\alpha}{\lambda_{2}}\right)^{2} = \frac{4r^{2}(t)\sin^{2}\alpha}{\lambda^{2}},$$
(5)

and therefore represents a fractional measure of grain boundary decohesion. At A(t) = 1 there is 100% linear (not areal) decohesion where the boundary of each cavity touches the adjoining cavities.

2. Updated DCCG Modeling

From Eq. 5,

$$\mathbf{r}(t) = \frac{\lambda \sqrt{\mathbf{A}(t)}}{2\sin\alpha}.$$
 (6)

If Eqs. 1 and 5 are combined, then it is possible to uniquely evaluate A_i , the function A(t) evaluated at $r = r_c$, which defines the measure of initial decohesion of a given grain boundary surface as a result of the equilibrium nuclear cavities, A_i :

$$A_{i} = \frac{4rc^{2}\sin^{2}\alpha}{\lambda i^{2}} = \frac{4\sin^{2}\alpha}{\lambda i^{2}} \left(\frac{2\gamma}{\sigma_{a}}\right)^{2} = \frac{16\gamma^{2}\sin^{2}\alpha}{\lambda i^{2}\sigma_{a}^{2}}.$$
 (7)

As shown previously,^{1,6} the increase in the area fraction of decohesion with time at the grain boundary, A(t), caused by DCCG can be found by satisfying the following equation:

$$\int_{A_1}^{A} \frac{dA}{f(A)} = \int_{a}^{b} G(t)dt,$$
(8)

where the functions f(A) and G(t) are defined below in Eqs. 9 and 34.

Both References 1 and 21 derive the following value for f(A,r):

$$f(A,r) = \left[\left(\frac{1}{\sqrt{A}} \right) \frac{\left(1 - \frac{r_{c}}{r}\right)(1 - A)}{\left[\frac{1}{2} Lr(\frac{1}{A}) - \frac{3}{4} + A(1 - \frac{A}{4}) \right]} \right].$$
(9)

The r_r term can be replaced using the relationship developed from the definition of A (Eq. 5)

$$r_{c}/r = (A_{i}/A)^{0.5}$$
 (10)

which makes f purely a function of A:

$$f(A) = \left[\left(\frac{1}{\sqrt{A}} \right) \frac{\left(1 - \sqrt{A_{1/A}} \right) (1 - A)}{\left[\frac{1}{2} Ln \left(\frac{1}{A} \right) - \frac{3}{4} + A \left(1 - \frac{A}{4} \right) \right]} \right].$$
(11)

The time-dependent notation, (t), is left out of A(t) in the above equations to reduce their written complexity; however, the time dependency —actually, the intervention of the time history of temperature and stress contained in G(t)—does remain. In prior studies, many assumptions have been made for determining the values of the parameters used in the above equations in an effort to integrate dA/f(A). The most difficult values to establish physically have been the initial cavity spacing, λ_i , and the resulting initial area fraction of decohesion A_i . By using the formulation in Eq. 7, this problem is reduced to defining λ_i for a given constant normal stress, σ_n .

One of the problems in assuming a value or values for the initial cavity spacing is that there is not a large experimental data base for cavity spacing, particularly in the general sense that would permit application across a broad range of materials.

A commonly used approach in previous studies^{1,5,6} has been to assign specific and constant values to either, and sometimes both, λ_i and A_i . Such assignments can only be generally related to the actual material and temperature and stress conditions of concern and tend to introduce a first-order artificial effect into the results. For example, in the original DCCG model,¹ λ_i was assigned a fixed value of 10 µm based on a limited study of unirradiated and annealed Zircaloy.^{8,9} As part of this study, it was reported that DCCG conditions produced λ_i values of 10-20 µm¹; the 10-µm value was selected for the original DCCG model as a conservative assumption (for lack of additional data). (Zircaloy cladding, as used in fuel rods in light water reactors, often has grains of about 10 µm or smaller in diameter.¹⁹) As noted in Section 1.1, the applicability of this specific Zircaloy data^{8,9} has been separately questioned.¹¹

As can be seen from Eq. 7, the initial value of A_i would appear to increase as either the normal stress, σ_n , or the initial cavity spacing, λ_i , decreases. This relationship between A_i and both λ_i and σ_n does make sense when taken in conjunction with the fact that, with decreasing stress, the probability of the development of a nuclear cavity likewise decreases, causing a corresponding increase in λ .

Unfortunately, as noted above, most previous studies assumed a constant initial cavity spacing. It would be more sensible to determine both the initial cavity spacing, size, and finally, the cavity growth from actual initial conditions. This cannot be done and an artificial skew in the results is introduced if the values for a critical cavity nucleus and an initial cavity spacing are independently selected (fixed) and then used directly to establish the initial area fraction of decohesion. For example, the approach used in Reference 6 assumed a critical nucleus radius of 0.01 μ m and parametrically varied the value of λ_i in order to evaluate the integration of Eq. 8. The previous DCCG model¹ used another approach of assuming a constant λ and an artificial value of A_i , while fixing the stress level. This approach, combined with a conservative bias in selecting material parameters, resulted in an evaluation which, overal¹, λ^{ns} intentionally

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conservative. However, these approaches cannot be used if one chooses to compute the critical radius, r_c , and the associated critical nucleus spacing, λ_i .

It is necessary to return to the basic theory of cavity nucleation to establish a more rational approach for defining λ_i .

One method for defining λ_i is to start with the fundamental expression for the change of free energy of the cavity nucleation system, ΔG :

$$\Delta G = \gamma S_v - \gamma_v S_v - V_v \sigma_v, \qquad (12)$$

where:

 S_v is the surface area of the cavity (m²);

 S_b is the surface area of the grain boundary displaced by the cavity (m²);

 γ is the surface tension of the material (N/m or J/m²);

 γ_b is the grain boundary interface force (N/m or J/m²);

 σ_n is the normal stress across the grain boundary (N/m²);

 V_v is the volume of the void or cavity (m³).

The probability of forming a stable nuclear cavity, P_N, can be expressed as follows:

$$P_{\rm N} = e^{-\Delta G^*/kT}, \qquad (13)$$

where:

ΔG* is the minimal free energy of a stable nuclear cavity evaluated from the derivative of Eq. 12 (J);

k is Boltzmann's constant (1.3806 J/K); and

T is the absolute temperature (K).

By evaluating Eq. 13 in conjunction with Eq. 12, it can be seen that, sensibly, at low stress levels there should be few cavity nuclei spaced far apart. As a result, A_i should be low and λ_i correspondingly high.

2. Updated DCCG Modeling

The importance of properly evaluating λ_i for predicting spent nuclear fuel rod lifetimes lies in the expected typical characteristics of dry storage cask thermal conditions.

Since the spent nuclear fuel assemblies are initially retained in the relatively cool spent nuclear fuel storage pools until ready for dry storage, the peak cladding temperatures have been relatively low since completing reactor irradiation. Once placed in dry storage casks, the nuclear fuel assemblies reach peak cladding temperatures that typically meet or exceed previous maximum cladding temperatures, which would have occurred during reactor operations (about 320 to 370°C¹¹). In addition, because of fuel rod prepressurization during fabrication, plus any fission gases released to the free volumes of the fuel rod, internal pressures of spent nuclear fuel rods are high. During reactor operations, it is expected that fuel rod internal pressures would come close to, but should still be less than, the reactor operating pressures (about 7 MPa for a BWR to upwards of 16 MPa for a PWR¹¹). Therefore, fuel rod cladding stress would be at a maximum in the dry storage casks where both the fuel rod peak cladding temperatures are high, similar to the reactor conditions, yet the ambient pressures are well below the reactor conditions, typically at about one atmosphere (about 0.1 MPa).

As a result, it is expected that the thermal contribution to the initial nuclear cavity distribution in the Zircaloy cladding and the ensuing thermal movement of these vacancies to grain boundaries (and hence to nuclear cavities) probably would be defined by the initial combined stresstemperature conditions of the dry storage casks.

In addition, residual vacancies formed from all prior histories—earlier designated as initial vacancies and arising from all phases of fabrication and from reactor operations (such as irradiation damage and possible added stress-temperature effects)—would be induced to thermally migrate to grain boundaries. At the grain boundaries, added cavities formed over the reactor operating history should already exist as a result of progression of vacancies transiently formed by the same irradiation damage and possible added to an increased cavity population of possibly increased individual sizes, resulting in an increased value for A_i and a reduced value for λ_j .

As can be seen in Eq. 12, it is necessary to evaluate the surface area of the cavity, S_v ; the surface area of the grain boundary displaced by the cavity, S_b ; and the volume of the cavity, V_v .

Since the cavity is assumed to be composed of two mirror-image segments of a sphere, the surface area of the cavity, referring to Figure 2.1, is

$$S_v = 4\pi r^2 [1 - \cos\alpha]. \tag{14}$$

2. Updated DCCG Modeling

The grain boundary surface displaced by the cavity is

$$S_{\rm b} = \pi r_{\rm b}^2 = \pi r^2 \sin^2 \alpha \,. \tag{15}$$

The volume of the cavity is

$$V_{r} = (2/3)\pi^{3} (2 - 3\cos\alpha + \cos^{3}\alpha).$$
 (16)

Substituting these equivalents into Eq. 12 gives

$$\Delta G = 4\pi r^2 \gamma (1 - \cos \alpha) - \pi r^2 \gamma_* \sin^2 \alpha - (2/3)\pi r^3 (2 - 3\cos \alpha + \cos^3 \alpha).$$
(17)

Minimizing ΔG , as ΔG^* , by taking the derivative with respect to r and equating the result to zero, gives the critical radius of the nuclear cavity as

$$r_{c} = \frac{4\gamma(1-\cos\alpha)-\gamma,\sin^{2}\alpha}{\sigma_{n}(2-3\cos\alpha+\cos^{3}\alpha)}.$$
(18)

If this critical value of the radius, r_c , is substituted into Eq. 12, the corresponding free energy change to establish a stable nucleus is

$$\Delta G^* = \frac{\gamma^3}{\sigma_s^2} F\left(\frac{\gamma_s}{\gamma}\right),\tag{19}$$

where

$$F\left(\frac{\gamma_{\star}}{\gamma}\right) = 16\pi^2 (1 - \cos\alpha) - \left(4\pi\sin^2\alpha\right) \left(\frac{\gamma_{\star}}{\gamma}\right) - \frac{16\pi}{3} \left(2 - 3\cos\alpha + \cos^3\alpha\right). \tag{20}$$

The probability of forming a stable thermally-induced nuclear cavity can be determined by evaluating ΔG^* from Eqs. 19 and 20 and incorporating it into Eq. 13,

$$P_{\mu} = e^{\left[-\left(\frac{\gamma^{3}}{kTon^{2}}\right)f\left(\frac{\gamma b}{\gamma}\right)\right]}.$$
(21)

It is apparent from Eq. 21 that the probability of forming a stable cavity nucleus decreases when stress decreases (with the logical probability of zero at zero stress) and as the free surface energy increases. In any event, since cavity nucleation is due to a coalescence of vacancies, the initial total volume of the cavity nuclei is, in practice, necessarily limited primarily by the vacancy concentration near the grain boundary. This result occurs because of the substantially higher

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vacancy diffusion coefficient within the grain boundary, D_{gb} , versus the bulk grain vacancy diffusion coefficient within the bulk grain, D_v . Effectively, once vacancies migrate from the bulk of the grain to the grain boundary, they can migrate more rapidly along the grain boundary to a cavity.

As introduced below in Eqs. 24 and 25, in its purest and simplest form, the vacancy concentration, $N_v(T)$, can be expressed as a function of temperature (although, as discussed in Sections 1.2 and 2.1 and later in Sections 3 and 4, the vacancy concentration may be a function of other parameters such as presence of foreign (alloying) atoms or irradiation damage that can cause distortions of the grain matrix). Cavity growth beyond the nuclear cavity depends upon a net gain of vacancies collected in the cavity. This gain comes from a positive imbalance of vacancy formation (or initial presence) and the diffusional path from the grain matrix to the grain boundary to the originally stable nuclear cavity versus a loss of vacancies from the cavity. This process can be described by growth equations. In addition, the creation of further cavity nucleation sites is possible with sufficient formation and diffusion of vacancies both within and to the grain boundary.

As can be seen in Eq. 21, there is a lower probability of forming stable cavity nuclei with decreasing stress. When this process is combined with a material that has either or both a large surface energy (essentially equivalent to surface tension²⁰) and the more dominant energy of vacancy formation, ΔE_v (introduced below in Eq. 25), then the number of vacancies generated from thermal sources only (ignoring other vacancy contributions), and available to form initial, stable cavity nuclei can be limited. As a result, the number of initial thermally-induced cavities under these conditions would be small. If thermally-induced vacancies are the sole source of vacancy generation, then spacing between nuclear cavities would be predicted to be relatively large even though the critical radius of the initial cavity may also be relatively large.

We can define the initial cavity spacing, λ_i , as the square root of the grain boundary surface area per stable nuclear cavity, A_o , expressed by

$$\lambda_{i} = \left(A_{o}\right)^{1/2}$$

where

$$A_o = V_v / C_{v_A} \Omega$$

and

(22)

(23)

2. Updated DCCG Modeling

$$C_{VA} = N_V \rho A_V d/M$$

where

 V_v is the volume of the cavity nucleus (m³);

C_{VA} is the grain boundary surface vacancy density (vacancy/m²);

 Ω is the atomic volume (1/m³);

 N_v is the vacancy density in the matrix (vacancy/atom);

 ρ is the density of the material (kg/m³);

- A_v is Avogadro's number (atoms/kg-mole);
- M is the molecular weight (kg/kg-mole); and
- d is a characteristic distance representing the grain volume associated with the vacancies
 - available for initial cavity nucleation at the grain boundary, which is assumed to be equal to twice the height of the spherical cavity segment (m) (see Figure 2.1).

For the simplest (purest) condition of only thermally-induced vacancies, these terms are further defined as follows:

$$N_{\nu}(T) = N_{0} e^{-\Delta E_{\nu}/kT} \quad (\text{Reference 20}) \tag{25}$$

and

$$d = 2r_c(1 - \cos \alpha) \tag{26}$$

where ΔE_v is the energy of formation of a vacancy (J/vacancy) and N_o is a temperaturedependent base vacancy density in the grain matrix. In the opinion of the authors, the value of N_o can be taken as a constant equal to the value of e (2.718....) since N_o is in the form of e^x and it is believed that x is very nearly equal to one for all materials. Others assign higher values for N_o of about 10²⁰ or 5 to 50.²¹ For purposes of this report, the value equal to e (2.718....) will be used.

The actual term for the total population of vacancy densities, N_{VTotal}, is probably much more complex than presented in Eq. 25. Potentially, as schematically indicated in Eq. 27:

(24)

 $N_{VTotal} = N_v(T) + N_v(alloy atoms) + N_v(fabrication processes)$

+ N_v (irradiation history) + N_v (irradiation damage)

+ N_v(added stress effects)

where

- $N_v(T)$ is the temperature-dependent vacancy density in the matrix, which, as a minimum, would come from Eq. 25, but could be of a more complex temperature-dependent nature;
- N_v (alloy atoms) is the possible initial contribution to vacancy density in the matrix resulting from lattice distortions caused by the presence of alloy atoms;
- N_v(fabrication processes) is the possible initial contribution to vacancy density in the matrix resulting from lattice distortions caused by the residual effects of the Zircaloy cladding fabrication processes;
- N_v (irradiation history) is the possible initial contribution to vacancy density in the matrix resulting from lattice distortions caused by the temperature-stress variations during the irradiation history;
- N_v(irradiation damage) is the possible initial contribution to vacancy density in the matrix resulting from atomic displacements and lattice distortions caused by the physical effects of irradiation damage; and
- N_v(added stress effects) are the possible initial and continuing contributions to vacancy density in the matrix resulting from a more complex dependency on stress effects than shown in Eqs. 24 and 25 (as discussed below in Section 3, some actual DCCG data indicate this possibility).

The terms noted above as possible initial contributors to vacancy density would be generated throughout the history prior to dry storage and would be evaluated at T_0 and t_0 , referring to the initial dry storage temperature and time conditions. As added effects, these same possible initial contributors to vacancy density would be, again throughout the history prior to dry storage, possible contributors to an increased grain boundary cavity population and/or cavity size in the irradiated Zircaloy.

For practical purposes, the development of the improved model for DCCG being described in this report will be presented as if thermally-induced vacancies are the only source of grain matrix

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(27)

vacancies. However, the reader should keep in mind that the vacancy density calculation should incorporate additional contributions along the line of Eq. 27; and that N_v in Eq. 24 should be replaced by N_{VTotal} . Yet, the current state of knowledge of irradiated Zircaloy prevents even a good estimate of the non-thermal contributions of Eq. 27 to N_{VTotal} .

However, it is now possible to restate the initial area fraction of decohesion, A_i , in terms of A_o , the grain boundary surface area per stable nuclear cavity (m²), by combining Eqs. 7 and 22.

$$A_i = \pi r_c^2 \sin^2 \alpha / A_{\sigma}.$$
 (28)

Under these assumptions,

$$A_{o} = \frac{\binom{2}{3}\pi r_{c}^{3}(2 - 3\cos\alpha + \cos^{3}\alpha)}{\binom{N_{v}\rho A_{v}}{M}2r_{c}(1 - \cos\alpha)\Omega} = \frac{\pi r_{c}^{2}(2 - 3\cos\alpha + \cos^{3}\alpha)}{3\binom{N_{v}\rho A_{v}}{M}(1 - \cos\alpha)\Omega}$$
(29)

or

$$A_o = K r_c^2 \tag{30}$$

where

$$K = \frac{\pi \left(2 - 3\cos\alpha + \cos^3\alpha\right)}{3\left(\frac{N_v \rho A_v}{M}\right)(1 - \cos\alpha)\Omega}$$
(31)

and

$$A_{i} = \frac{\pi rc^{2} \sin^{2} \alpha}{K rc^{2}} = \frac{\pi \sin^{2} \alpha}{K}.$$
(32)

Now, A_i is not dependent upon r_c . This indicates that the initial area fraction of decohesion is not directly dependent upon the stress level. It is, however, at least dependent upon temperature through its relationship with N_v, the vacancy concentration and, as noted in Eq. 27 (N_{VTotal}), is probably a function of several other parameters. A_i is also dependent upon both the surface tension, γ , and the grain boundary interface force, γ_b , to the extent that the dihedral angle, α (Eq. 2), is a function of the ratio of the grain boundary interface to the free surface forces (both forces ca., have a very mild temperature dependence^{7,20} which tends to cancel out and otherwise can be ignored). The ratio of γ_b to γ , used in the calculation of α , has been accepted as about 1/3 to

1/2.1.6.7 Therefore, A_i appears to be, for practical purposes, a function only of the temperature with the caveat noted above regarding N_{VTotal}.

The cavity spacing, λ_i , on the other hand, is a function of both K and r_c (from Eqs. 22, 30 and 31), which are, in turn, functions of both the temperature, through N_v (again with the N_{VTotal} potential effect), and the normal stress applied to the grain boundary surface in addition to the surface and grain boundary interface forces (again through α).

$$\lambda_i = \sqrt{A_o} = \sqrt{Kr_c} . \tag{33}$$

Using the above relationships and knowing the conditions of temperature and normal stress, it is now possible from these conditions and basic material parameters to uniquely calculate the minimal and maximal values for A_i and λ_i respectively (the temperature-dependent contribution to N_v). This approach thereby avoids the need to introduce possible artificial first-order effects in evaluating Eq. 8 by the need to assume values for either or both of these variables. At the same time, the approach is limited by a lack of ability to calculate N_{VTotal} . However, if it were possible to completely account for all effects in N_{VTotal} , then it would provide a more complete definition of A_i and λ_i ---still avoiding the artificial effects of assuming values for these variables.

With the ability to define A_i , it is now possible to calculate the term f(A) of Eq. 11 and proceed with the evaluation of the integral defined on the left side of Eq. 8. The integral defined on the right side of Eq. 8 involving G(t) retains the same definition as that in the original DCCG model.¹

$$G(t) = \left(\frac{32}{3\sqrt{\pi}}\right) \left(\frac{F_g^{3/2}(\alpha)}{F_v(\alpha)}\right) \left(\frac{\Omega\sigma_n}{k\lambda^3}\right) \left(\frac{\partial D_{gb}(T)}{T(t)}\right),$$
(34)

where

$$F_{\rm g} = \pi \sin^2 \alpha \tag{35}$$

is the displaced grain boundary area function⁶ (obtained from Eq. 15 by dividing by r^2);

$$F_{\nu} = \left(\frac{2}{3}\right)\pi\left(2 - 3\cos\alpha + \cos^3\alpha\right) \tag{36}$$

is a cavity volur = 'ut ction⁶ (obtained from Eq. 16 by dividing by r^3);

δ is the thic is of the grain boundary which is typically taken as about 1 nm (10 Å) or less^{1,22} (m); e. c

(37)

 D_{gb} is the grain boundary diffusion coefficient (m²/sec);

other terms are previously defined.

The grain boundary diffusion coefficient, D_{gb} , differs from and is greater than the bulk diffusion coefficient, D_v . It tends to vary with the square root of D_v .²² To avoid the need to specifically assign a value for the grain boundary thickness, δ , the term δD_{gb} (m³/sec) is often used and experimentally determined as an entity called the grain boundary diffusion parameter, P.²²

As is the case for D_v , D_{gb} can be expressed with the standard exponential temperature dependency:

$$D = D_{e} e^{-Q_{D}/RT}$$

where

D is the temperature-dependent diffusion coefficient (m2/sec);

 D_0 is the base (pre-exponential) diffusion coefficient (m2/sec);

Q_D is the activation energy for the diffusion process (kJ/kg-mole); and

R is the universal gas constant (8.3143 kJ/kg-mole-K).

2.2 Input parameters for the DCCG model

The purpose of this section is to provide recommended values for the material-dependent variables required to solve the equations in Section 2.1 as applied to a Zircaloy system containing α -zirconium—i. e., zirconium with the hexagonal-close packed (HCP) crystal structure consistent with the temperatures of interest to dry storage (which are well below the full α - β transition at about 1140 K). In many instances, the material properties are for elemental zirconium (and often, the data are from experiments on a single crystal grain of α -phase zirconium) because the actual data for Zircaloy was not found. The presentation of variables generally will parallel their order of introduction in Section 2.1.

As an added caveat, the authors were unable to find any data for the following parameters for either zirconium or Zircaloy in the irradiated condition, let alone the equivalent to the high neutron fluence typical of sucht fuel cladding.

2.2.1 Es or γ The surface energy or tension of the material (J/m² or N/m)

The surface energy, E_s , or surface tension, γ , is a difficult parameter to evaluate experimentally. However, two theoretical formulations were found for calculating the free surface energy. From Cottrell²⁰ there was the following formulation:

$$\gamma = \left(\frac{1}{3}\right) r_a h_{fv}, \qquad (38)$$

where

 r_a is the atomic radius (m) and

 h_{fv} is the volumetric heat of fusion (J/m³).

Lawn and Wilshaw²³ presented a second formulation for free surface energy:

$$\gamma \approx \text{Eb} / \pi^2, \tag{39}$$

where

E is Young's modulus (N/m^2) and

b is the Burgers vector, which is essentially the inter-atomic spacing²⁰ (m).

The evaluation of the first surface energy formulation by Cottrell used data for zirconium for h_{fv} by Samsonov²⁴ and assumed that r_a was half of the lattice measurement "a" from Hultgren²⁵ (see Subsection 2.2.4 below). The result was a far smaller value for γ equal to about 2.2 J/m² than the only other value found to be reported for Zircaloy (an un-referenced value of 35 J/m² ^{14,15}, a value also used in the original DCCG model¹).

Evaluating the second surface energy formulation by Lawn and Wilshaw involved use of data for Young's modulus for Zircaloy. Values for Young's modulus were taken from both the United States Nuclear Regulatory Commission (USNRC) thermal properties document MATPRO²⁶ (including the temperature effect), and another source for pure zirconium.²⁷ The Burgers vector, b, was assumed identical to the lattice measurement "a." This resulted in values for γ of about 2.6 to 3.1 J/m² with the more appropriate MATTCO (Zircaloy) values ranging from 2.6 to 3.0 J/m² based on considerations of both temperature in d anisotropicity. As a result, the following interim value of γ is recommended for the temperature of Zircaloy DCCG interest:

$$\gamma \approx 2.8 \mathrm{J} / \mathrm{m}^2$$

(40)

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This value is consistent with the values of γ presented for both α -iron and γ -iron, copper and nickel in Riedel ($\gamma = 1.7-2.1 \text{ J/m}^2$)⁷; but, as noted above, it is substantially below the value of 35 J/m² presented by Chin et al.^{14,15} that was used in the first DCCG model.¹

2.2.2 γ_b Grain boundary interface force of the material (J/m² or N/m)

As noted in Section 2.1, the ratio of γ_b , the grain boundary interface force, to γ has been accepted as a ratio of about 1/3 to 1/2.1,6,7 Therefore, the value of γ_b will be taken as

$$\gamma_b \approx 1.0 \text{J/m}^2 \text{ or } \approx 1.4 \text{J/m}^2. \tag{41}$$

The first value for γ_b (1.0 J/m²⁾ compares well with values of 0.65-0.85 J/m² reported by Riedel for α -iron, copper and nickel (which did have an average ratio of about 3/8 compared to the accompanying values for γ); whereas the second value (1.4 J/m²⁾ is consistent with the 0.5 γ assumption of the original DCCG model.^{1,6} The latter value (the 0.5 γ assumption) is recommended, for purposes of this report, to be consistent with prior DCCG modeling. The effect of choosing a value for γ_b is most noticeable in the evaluation of α , the intersection angle between the cavity spherical surface and the grain boundary.

2.2.3 σ_n Normal stress across the grain boundary (N/m²)

The normal stress across the grain boundary typically has been interpreted as the local hoop stress in the Zircaloy cladding caused by fuel rod internal pressure minus the external pressure.

The internal pressure in a fuel rod primarily consists of the combined sum of the initial fabricated pre-pressurization with helium (typically 1-3 MPa in modern water reactor nuclear fuel rods) plus any contribution from gaseous fission products released as a result of the power history of the fuel rod. The actual internal pressure must be evaluated at dry storage fuel rod free volume weighted temperatures. For conservative purposes, that temperature should be identical to the peak fuel rod cladding temperature for the dry storage conditions unless the fuel rod plenum temperature can be more accurately determined and a proper mixed-mean volumetric average temperature for all of the free volumes within the fuel rod(s) can be determined accurately.

Reference 11 makes a fairly reasonable argument that a worst-case (PWR) spent fuel rod internal pressure, considering both maximum pre-pressurization and relatively severe gaseous fission products release would lead to a peak fuel roc internal pressure of about 16 MPa at 370°C. This internal pressure translates into a cladding hocp creates about 130 MPa or less (Figure 2.2 of Reference 11) for dry storage cask conditions where the spent fuel rods face an ambient pressure

of one atmosphere (0.1 MPa). Based on this argument, for the purposes of general application of DCCG modeling to spent nuclear fuel dry storage, a nominal maximum hoop stress level of 130 MPa is recommended.

2.2.4 δ Grain boundary plane thickness (m)

The grain boundary plane thickness is usually assumed to be two to three atom diameters.²⁸ This assumption is essentially equivalent to two to three Burgers vectors. As noted above for zirconium, the Burgers vector is effectively the lattice measurement "a,"²⁵

$$b = a^* = 3.2323 \text{ \AA},$$
 (42)

which results in a grain boundary plane thickness of about 6.5 to 9.7 Å. The latter value (10 Å) was used in the previous DCCG model.¹ In Reference 22 (Vieregge and Herzig), which is the basis for the definition of D_{gb} , the grain boundary plane thickness is taken as a slightly smaller value of 5 Å. Because of this uncertainty, and the fact that Vieregge and Herzig report both experimental and analytical forms for P which is δ times D_{gb} , the grain boundary plane thickness will be assumed as

$$\delta = 5 \mathring{A} = 0.5 nm \tag{43}$$

to be consistent with the definition of Dgb in the Vieregge and Herzig paper. However, since both the formulation of G(t) in Eq. 34 contains the only needed definition of δ in the form of P (i.e., δD_{gb}), and the Vieregge and Herzig formulations for P will be used in this report, the specific value of δ is no longer of any consequence.

2.2.5 D_V Bulk grain diffusion coefficient within the grain boundary (m²/sec)

There has been a substantial increase in the data bank on bulk self-diffusion in zirconium since the original DCCG model was published, e.g., References 22 and 29 through 31. In particular, the data on and approach used for defining the related bulk grain self-diffusion and grain boundary coefficients, D_v and D_{gb} (presented in Reference 22) are used to update the diffusion correlation used in the original DCCG model.^{1,32}

Recalling Eq. 37 as the general form for the temperature dependence of a diffusion coefficient, Vieregge and Herzig²² make the following arguments.

- The single-crystal zirconium bulk self-diffusion data collected by Horvath et al.²⁹ is probably some of the best collected to date because of the truly microscopic experimental data collection technique used (laser-caused sputtering to remove atomic layers).
- 2) Their bulk self-diffusion data, collected over a wide temperature range (619-1127 K) on poly-crystalline zirconium was substantially higher than the single crystal data (by multiple orders of magnitude). However, their data was still typically well below much of the other data that generally resides in the inappropriate temperature range of 1000 K to the α-β transition at about 1140 K (e.g., References 30 and 32).
- 3) Based on their microscopic examinations of poly-crystalline zirconium samples, arrays of dislocations form on the grain boundaries resulting in enhanced flux of atoms away from and, hence, vacancies towards the poly-crystalline grain boundaries.

As a result, the poly-crystalline effective bulk self-diffusion (Dveff) data is substantially enhanced over the Horvath et al. single crystal zirconium bulk self-diffusion data.

In Reference 30, de Svarch and Rodriguez make a sensible argument that the reason the highertemperature bulk self-diffusion data (above 1000 K) is substantially higher than the Horvath et al. data and, although not noted, also well above the Vieregge and Herzig data, is that small amounts of β -zirconium begin to form at the grain boundaries at temperatures above 1003 K. Because of the continuous nature of the grain boundaries and the fact that β -zirconium has a D_v about five orders of magnitude above that for α -zirconium, a small amount of β -zirconium being present dramatically increases the observed α -zirconium D_v. However, since the precursory β zirconium formation only occurs at temperatures substantially above those of interest for spent fuel rod dry storage conditions, these data on D_v can be ignored.

Therefore, the Vieregge and Herzig data for the effective bulk self-diffusion (Eq. 3 of Reference 22), is recommended as a basis for the temperature range of Zircaloy DCCG interest:

$$D_{\text{veff}}(T) = D_{\text{veff}0} e^{-Q_v/RT}$$
(44)

where

$$D_{\rm veffo} = 1.0 \times 10^{-10} \,\mathrm{m}^2 \,/\,\mathrm{sec} \tag{45}$$

and

$$Q_{\rm u} = 139 \pm 27 \text{kJ} / \text{kg} - \text{mole}$$
 (46)

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2.2.6 D_{gb} Vacancy diffusion coefficient within the grain boundary (m²/sec)

The vacancy diffusion coefficient within the grain boundary, D_{gb} , is related to the square root of the bulk grain self-diffusion coefficient.^{22,33} Using this relationship leads to a relationship for P, the grain boundary diffusion parameter, which is identical to the product δD_{gb} . The correlation for P is presented in the next subsection. Once P is obtained, D_{gb} can be simply calculated:

$$D_{gb} = \frac{P}{\delta}.$$
 (47)

2.2.7 δD_{gb} (P) Vacancy diffusion parameter within the grain boundary (m^3 /sec)

The correlation for the effective vacancy diffusion parameter within the grain boundary, P_{eff} or δD_{gbeff} , also comes from Vieregge and Herzig (Eq. 4 of Reference 22):

$$P_{eff}(T) \equiv \delta D_{sbeff_0} = P_{eff_0} e^{-Q_r/RT}$$
(48)

where

$$P_{effo} = \left\{ 4.2^{+5.9}_{-2.5} \right\} \times 10^{-13} \,\mathrm{m}^2 \,/\,\mathrm{sec}$$
⁽⁴⁹⁾

and

$$Q_{p} = 167 \pm 7 \text{kJ} / \text{kg} - \text{mole}.$$
 (50)

As a potentially significant contributor to the argument that other factors can affect vacancy and cavity densities, Vieregge and Herzig have an interesting note in Figure 4 of their paper, which presents the data behind the curve fit for P_{eff} presented in Eq. 48. In that note, they state that the data at their lower temperature limits—619 K to about 750 K, or 346 °C to about 477 °C, very appropriate for dry storage conditions—are "...enhanced values and result from untypical grain boundary diffusion profiles due to strong impurity segregation." This enhancement is over two orders of magnitude at the lower temperature of 346 °C and appears to be leveling out with decreasing temperature. From Eq. 34, it can be seen that this effect on P_{eff} (δD_{gb}) would equally affect G(t) and also its integral value in Eq. 8.

Since the test specimens in this paper were nominally pure zirconium, the level of potential impurities (i.e., non-zirconium atoms) would be far less than would be present in Zircaloy with its $\approx 2\%$ non-zirconium alloying atoms. Therefore, it is possible to hypothesize that the effect on Zircaloy would be even greater than that noted above.

2.2.8 Ω Atomic volume of the material (1/m³)

The atomic volume of a zirconium atom has been reported as ranging from $2.31*10^{-29}$ to $3.37*10^{-29}$ m³/atom.¹ The latter value was used by Chin et al.^{14,15} and is simply the cube of the lattice measurement "a." However, by: 1) using the basic calculation involving Avogadro's number, the molecular weight and density or 2) calculating the volume directly from the "a" and "c" lattice measurements for zirconium²⁵,

$$a = 3.2323$$
Å (51)

and

$$c = 5.1477 \text{ \AA}$$
, (52)

the correct atomic volume of a zirconium atom and the value used in this report should be

$$\Omega = 2.33 * 10^{-29} \, m^3 /_{atom}. \tag{53}$$

2.2.9 No Base value for thermally-induced vacancy density in the matrix (vacancy/atom)

The base value for the thermally-induced vacancy density in the matrix (N_0 in Eq. 25) for Zircaloy comes from basic thermal-physics considerations and is the value e raised to a power that is material-dependent. However, as noted above, the authors believe that value is always near unity regardless of the material. Hence, for purposes of this report, the value of N_0 is e raised to the essentially first power, or

$$N_0 \equiv 2.718$$
. (54)

Other reported values for N₀ are about 10^{20} and from 5 to $50.^{21}$ The spread in these values warrants further study.

2.2.10 DE_v Base case value for energy required to form a new vacancy in the matrix (ev/atom)

The most significant new variable introduced in the updating of the DCCG modeling is the energy required to form a new vacancy, ΔE_v , within the matrix of a material.

The primary reason for the significance of ΔE_v is its location in the exponential term that defines the thermally-induced vacancy density in the matrix (Eq. 25). As long as the thermal contribution is the only effect supplying vacancies to N_{VTotal} (Eq. 27), then a small change in this variable

can have a profound impact on the prediction of DCCG lifetime-limiting conditions. The ramifications of this effect are discussed briefly below and in more detail in Sections 3 and 4.

There are several ways of calculating ΔE_v^{33-38} for pure elements. With difficulty, ΔE_v can be experimentally measured, as it has been for several pure elements; for example, experimental values of ΔE_v for only 15 different elements were found in References 35-38. In Reference 35, Hood reports values of both experimental and calculated ΔE_v for α -zirconium. The experimental data indicates that ΔE_v would be a minimum of 1.5 ev/atom for α -zirconium, whereas the two calculated methods estimated the value as 1.8 to 1.9 ev/atom.

To further investigate the possible spread in the value of ΔE_v , the several methods, including the two noted in Reference 35, were applied by the authors for estimating ΔE_v . These methods produced values mostly between 1.5 and 2.9 ev/atom, one value at 0.95 ev/atom and one value, acknowledged as a rough overestimate, at 5.6 ev/atom.³⁶ For purposes of demonstration in this report, the minimum reported experimental value of 1.5 ev/atom for α -zirconium is conditionally recommended for Zircaloy.

As noted above, the selected value for ΔE_v profoundly affects the prediction of DCCG lifetimelimiting conditions if only thermal effects are considered. As the value of ΔE_v increases, the probability of developing thermally-induced DCCG cavity nucleation and/or growth dramatically decreases for a given stress-temperature condition. Because of this effect, great care must used in selecting a value for ΔE_v when calculating N_{VTotal} (Eq. 27) if using the updated DCCG model and only the thermally-induced vacancy generation [N_v (T) of Eqs. 25 and 27] to predict real-life irradiated Zircaloy DCCG behavior.

There are major differences, both microscopically and macroscopically, between irradiated Zircaloy and the idealistically pure α -zirconium. It is expected that most of those differences would disrupt the idealized HCP crystal lattice and grain boundaries, with the attendant probability of creating additional vacancies and, possibly, increasing the cavity population within the grain boundaries.

These lattice disruptions could be caused by fabrication processes (such as cold-working and heat treatments); the presence of almost 2-out-of-100 non-zirconium alloy atoms; both neutron and chemical effects resulting from irradiation; and possibly a more complex relationship with stress (than shown in Eqs. 1 and 34). These factors could increase the possibility of (1) more easily forming vacancies, because of increased lattice defects in the actual irradiated Zircaloy

crystal lattice (effectively lowering the impact of the actual value of ΔE_v), and (2) increasing the nucleation sites available for cavities to form on the grain boundaries.

As discussed below in Sections 3 and 4, other evidence of cavity spacing in pure copper does appear to confirm that the formulation for N_{VTotal} is more complex than the simple exponential thermally driven function for N_v (T) presented in Eq. 25.

2.2.11 ρ Density of the material (kg/m³)

The density of Zircaloy is based on that presented in MATPRO.²⁶ Considering the density as constant,

$$\rho = 6490 \frac{kg}{m^3}$$
 (55)

is a representative value for dry storage temperature conditions.

2.2.12 M Molecular weight (kg/kg-mole)

Since the commonly used zirconium alloys of Zircaloy-2 and Zircaloy-4 have only about 2% non-zirconium constituents, the standard international atomic weight for zirconium is a reasonable value (to within less than 1%) to represent the molecular weight of Zircaloy:

$$M = 91.22 \frac{kg}{kg - mole}.$$
 (56)

÷.

3. Comparison of original versus updated DCCG models

3.1 Comparative results between original versus updated DCCG models

The original DCCG model¹ used a set of material parameters to represent Zircaloy that was partially defined in that report. The updated DCCG model described in this report requires input values equivalent to all of these original Zircaloy material parameters (except for the defined fixed value for the initial cavity spacing, λ_i) plus several newly introduced parameters, such as the vacancy formation energy, ΔE_v . As part of the updating of the DCCG model, a concurrent literature search was performed with the dual objective of both updating all of the original material parameters plus finding definitive values for the new parameters. The results of the literature search are presented in Section 2.2. Table 3.1 presents a complete listing of the two sets of input parameters—the values taken from Section 2.2 compared to the original model. For the reader's convenience, Table 3.1 also includes a set of consistent units for use in the DCCG model.

3.1.1 Background for comparing model calculations

For purposes of directly comparing results from the original versus the updated DCCG model, it is desirable to have a simply defined stress-temperature condition. This approach avoids having the confusing impact of both defining or estimating a peak cladding temperature and resulting temperature and stress history, then attempting to separate from the results those effects that are strictly time-temperature related.

The stress-temperature condition chosen for model comparison can be stated as a problem: for a given set of time-constant stress conditions, what corresponding set of constant peak cladding temperatures would produce predictions of cladding failure at 20 years from the start of the constant stress-temperature conditions? For purposes of this report, the same failure criterion used in the original DCCG report, A = 0.15 (i.e., failure is assumed when A, the area fraction of decohesion, reaches 15%),¹ is maintained.

Using the parameters presented in Table 3.1 in the updated DCCG model immediately demonstrates the problems discussed in Section 2.2.10, i.e., regarding how the selected value for the energy required to form a new vacancy, ΔE_v for α -zirconium, profoundly affects the prediction of DCCG lifetime-limiting conditions. As noted in that section, a single experimental indication of the value of ΔE_v^{35} , plus several analytical forms for calculating ΔE_v , lead to values of at least 1.5 ev/vacancy (the experimental value). No values for ΔE_v for Zircaloy (versus α -

zirconium) were found in the material property literature research; nor were any analytical formulations for ΔE_v found that accounted for non-pure metals.

 ΔE_v is necessary for predicting a value for N_{VTotal}, the total vacancy density in the matrix (as defined in Eq. 27). With current knowledge, it is only possible to use the thermally-induced vacancy source, N_v(T) of Eq. 25, to represent N_{VTotal} as the nominal calculation for the updated DCCG model. As a result, when applied to the calculation for a 20-year lifetime with constant stress-temperature conditions, predictions for peak temperatures are substantially higher using the updated model than those from the original model.

These much higher peak temperatures are singularly due to the dramatic effect of ΔE_v , which appears in the negative exponent defining N_v(T). Even a 10% increase in ΔE_v can cause an order-of-magnitude decrease in N_v(T) which, in the current form of this updated DCCG model, is the ultimate and only producer of vacancies that diffuse to the grain boundaries and, hence, to the cavities on the grain boundaries.

Of the values for ΔE_v reported in Section 2.2.10, all but one are essentially idealistic and are for pure α -zirconium. As discussed earlier, the value of N_{VTotal} (Eq. 27) should not be so dependent on the selected value of ΔE_v . It should represent the far more complex microstructure of irradiated Zircaloy. These other factors beyond the ΔE_v contribution to N_{VTotal} need to be considered in a more realistic evaluation of the vacancy production in irradiated Zircaloy.

3.1.2 Comparative model calculations results

Considering other possible sources of vacancies (N_{VTotal}), the original DCCG model¹ is compared directly with the upgraded model as shown in Figure 3.1. The upgraded model, as defined in Section 2.1, used the Eq. 25 formulation for N_v(T) and the parameters as defined in Table 3.1 to produce the results in Figure 3.1 with one exception—a simple, constant-value multiplier was applied to N_v(T) after the exponential impact of ΔE_v had occurred. That is to say, a simple constant multiplier is placed in front of N_v in Eq. 24 of Section 2.1. The single value of this multiplier was then adjusted to (normalized to) the temperature prediction from the original DCCG model for a constant stress of 100 MPa.

Table 3.1 Comparison of updated versus original DCCG model parameters

1!sme_clature	Updated Model	Original Model	Units	Meaning of Parameter
α	75.522	.50.0 *	degrees	Intersection angle between the cavity void spherical surface and the GB.**
Coc'ne a	0.25000	0.642.79		
Sine α	0.96825	0.76604		
δ	5.00E-10	9.69E-10	m	GB plane thickness (not actually used in current model).
Ý	2.8	35	J/m ² or N/m	The surface tension or energy of the material.
Ъ	1.4	17.5	J/m ² or N/m	GB interface force of the material.
λί	Calculated	1.000E-05	m	Initial cavity spacing associated with Aj.
Ai	Calculated	Assigned		The function A evaluated at $r = r_c$ defining the initial decohesion.
b	3.2313	3.23	Å	Burgers vector taken as the lattice constant "a" for zirconium.
Ω	2.33E-29	3.37E-29	m ³ /atom	Atomic volume of the material (cube of Berger's vector in original model).
Nv	Calculated	**	vac/atom	Vacancy density in the matrix.
No	2.718		Vac/atom	Base (pre-exponential) vacancy density in the matrix.
ΔΕν	1.500		ev/vac	Minimum experimental energy of formation of vacancies for Zr.
ρ	6490	6550	kg/m ³	Density of the material.
. Ay	6.02E+26	6.02E+26	atoms/kg-mole	Avogadro's number.
M	91.22	91	kg/kg-mole	Molecular weight.
ď	Calculated		m	Characteristic distance for the vacancies associated with Cavity.
D _{vo}	1.00E-10	5.90E-06	m ² /sec	Base (pre-exponential) diffusion coefficient (used as Dgbo in original model).
$P_{gbo} = D_{gbo} * \delta$	4.20E-13	5.72E-15	m ³ /sec	Base (pre-exponential) GB diffusion parameter coefficient.
· Qv	139000	131000	kJ/kg-mole	Activation energy for the bulk self-diffusion (used as Qp in original model).
Qp	167000		kJ/kg-mole	Activation energy for the diffusion parameter in the GB.

* Value assumed in Reference 1 for added conservatism (violates the assumptions in Eq. 3).

** Grain Boundary

3. Comparison of Original Versus Updated DCCG Models



Figure 3.1 Comparizon to the original DCCG model and the normalized results from the updated DCCG model

Figure 3.1 (which covers a reasonable hoop stress range for dry-storage conditions), shows that this simple modification to the upgraded model produces results very similar to those of the original model. Granted, the multiplier seemingly is large—for this case, the value is 8*10⁸. However, this value must be viewed in perspective with some of the potential numbers associated with the possible matrix disruptive effects presented in Eq. 27. For example, just considering the following terms from Eq. 27:

- N_v(alloy atoms)—a single 10-μm diameter Zircaloy grain (as noted in Section 1, a size in the typical range for Zircaloy cladding) would contain about 1000 times that number (7*10¹¹) of non-zirconium atoms as potential grain matrix distortion and cavity initiation
 sites—and, as noted in Section 2.2.7, there are indications that these non-zirconium atoms would have a very notable effect on DCCG predictions;
- (2) N_v(irradiation damage)—as a direct result of the in-reactor neutron flux history, every one of the nearly 4*10¹³ atoms in that same 10-μm diameter Zircaloy grain would have been knocked out of its then current position in the grain matrix several times, each time creating what could be either short- or long-term vacancies, during a fuel rod irradiation lifetime.

3.2 Results from comparing updated DCCG model with non-zircaloy data

As noted in Section 1, DCCG has been observed to occur in some metals and alloys at conditions consistent with or similar to temperatures and stress conditions seen in spent fuel dry storage environments.^{12,13} These references contain specific data on the spacing (λ) of DCCG cavity populations. Another source is the questionable¹⁰ Zircaloy data of References 8 and 9.

Although References 12 and 13 are not Zircaloy data sources, they can be examined for the presence of parameters that affect cavity density and growth. References 8 and 9 do not, at this time, appear to be appropriate for this use.

3.2.1 Discussion of copper DCCG data

In Reference 12, Raj (one of the early proponents of the DCCG phenomenon⁶) performed DCCG experiments on bicrystals of copper. In these experiments, eight copper bicrystals were loaded with varying pairs of constant tension, perpendicular to the shared bicrystal grain boundary (normal stress), and constant temperarize for conditions that resulted in the development of cavities at the bicrystal grain boundary . of the eight experiments were classified by Raj as DCCG failures and the other the shared bicrystal grain boundary were evaluated in this report. At the completion of each experiment, the bicrystals were separated at their grain boundary and the exposed cavities of each bicrystal were characterized by single-valued measurements of cavity spacing. Unfortunately, there was no discussion regarding how the data was reduced to single values nor the associated uncertainties with these single values.

The experiments were performed at four each stress levels (1, 5, 10 and 13 MPa) and temperatures (600, 650, 700, and 750°C). Again, unfortunately, with 2 x 4 parameters spread over six tests, there was no consistent pattern across either parameter to test the full array. However, there were two mini-sets of three data each: 10 MPa at 650, 700, and 750°C and 1, 10 and 13 MPa at 700°C.

With this total data set in hand, the updated DCCG model described in this report was applied to the test conditions for this data set. To do this required tailoring the input material parameters to represent copper. This was accomplished using the same analytical approaches and same references used to determine the Zircaloy material parameters discussed in Section 2.2.

The results from this use of the updated model produced some interesting results.

- (1) The general trends of the model match those of the entire data set fairly well.
- (2) For the mini-set of constant 10 MPa stress at 650, 700, and 750°C, the model predicted cavity spacing to within 20% of the reported values, but with a lesser slope—i.e., 15% high for the 650°C test, less than 10% low for the 700°C test, and 20% low for the 700°C test; or a mild indication of a more complex temperature relationship in N_v(T) than that of Eq. 25.
- (3) For the mini-set of varying stress at 700°C, the model predicted cavity spacing to within 25% of the reported values for the two high-stress level tests at 10 and 13 MPa but overpredicted by a factor of six (i.e., fewer predicted cavities) for the very-low-stress level test at 1 MPa; an indication of a possibly strong dependence on normal stress as indicated in N_{VTotal} (Eq. 27).

These results are indicative of a need for a more complex dependency on both temperature and stress than represented by the simple exponential dependency on temperature in Eqs. 25 and 34, respectively (possibly an even more complex relationship with temperature than indicated for N_{VTotal} in Eq. 27).

3.2.2 Discussion of chromium-molybdenum steel DCCG data

Reference 13 presents some DCCG cavity formation data for chromium-molybdenum steel used in turbine rotors. The authors of that paper do state that they saw no temperature dependence in cavity distribution data. To support this conclusion, the authors refer to Figures 3 and 4 in their paper. Both figures are log-log plots, with Figure 3 presenting three data sets (containing two constant stress levels and three constant temperatures) of cavity areal density (cavities/unit area) versus time (out to several months). Figure 4 presents the same three data sets as cavity areal density versus creep (out to several percent creep—these are highly stressed tests).

In Figure 3, the authors present three linear curve fits (slope being the power law exponent), with different slopes for each data set. In Figure 4, the authors present a single linear curve fit (again, slope being the power law exponent) for all three data sets. In the accompanying text, the authors state that the results, cavity areal densities, are independent of temperature.

However, examination of Figures 3 and 4 of this reference raises some questions. In Figure 3, there appears to be definite and notable breaks in the slopes of two of the three data sets (those characterized as 550 MPa and 216°C and 600 MPa and 147°C)—indicating some unaccounted parameter affecting the results. In Figure 4, there appears to be definite differences in the slopes of the three data sets, particularly in the 600 MPa and 147°C set, with slope increasing with temperature—indicating that temperature is a parameter.

Because the data in this paper are only presented in figure form, data are not easily reduced for use in comparing these results to those from the updated DCCG model. This fact, plus the confusion about the stated lack of temperature dependency, has resulted in no modeling to date.

3.3 Comments on DCCG modeling improvements and model comparisons

What the above discussions and comparative modeling results indicate are that:

- (1) there was a need to improve on the original DCCG model to remove some artificial constraints, particularly fixed input parameters, that strongly affected predictions;
- (2) improvements have been made that place the DCCG modeling on a more firm thermalphysical basis;
- (3) coincidental with these modeling improvements, "verbares in the idealized pure metal thermal-physical approach were discovered, despite basis for DCCG

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modeling methodology for predicting possible lifetime limiting conditions for spent nuclear fuel rods during long-term dry storage:

- a) the introduction of a new input material parameter, the vacancy formation energy (ΔE_v) required to minimally determine N_v(T) (the vacancy density in the grain matrix, Eq. 25) absolutely dominated the prediction of Zircaloy lifetime limiting conditions;
- b) the approach ignored the potential contribution to N_v (N_{vTotal} of Eq. 27) from considering the reality of the microscopic damage that would exist in irradiated Zircaloy;
- (4) available data on cavity spacing in copper¹² and chromium-molybdenum steel¹³ indicates a need for a more complex dependency of the vacancy density in the matrix of a material, N_{VTotal}, on both temperature and stress;
- (5) the weakness in the Zircaloy data base is the current need to rely on:
 - a) limited experimental data and analytical correlations based on studies of pure materials, in general, and pure a-zirconium specifically, and all in the unirradiated condition;
 - b) limited and primarily unirradiated and short-term Zircaloy creep-related data for the study of long-term DCCG and creep-related behavior of irradiated Zircaloy.
- (6) Perhaps some of the weakness in modeling Zircaloy DCCG behavior indicates a need to revisit some of the basic assumptions of DCCG modeling^{1,5,6} such as the basic tenets that the cavities are:
 - a) true voids (no gas present), whereas actual spent fuel rods typically have internal pressures (differential pressures to ambient) of many MPa (many 100s psi) with the dominant pressurizing gas being the highly diffusive helium—internal pressure in the cavities from helium diffusing through the Zircaloy cladding would exacerbate DCCG damage;
 - b) composed of continuously growing mirror-image spherical surface segments—if the cavities progressively convert from the spherical segments to le ticular-shaped cavities (from mirrored bowl shaped to mirrored plate shape ") to n an equivalent collection of vacancies would also exacerbate DCCG damage.

Considering the comparison of the updated DCCG model to the Raj copper data and the apparent temperature dependency of the chromium-molybdenum steel tests, it follows that Eq. 27 should be modified as follows:

 $N_{VTotal} = N_{v1}(T) + N_{v2}(T) + N_{v}(alloy atoms)$

+ N_v(fabrication processes) + N_v(irradiation history)

+ N_v(irradiation damage) + N_v(added stress effects)

+ N_v (helium internal pressure) + N_v (cavity shape);

(58)

where

 $N_{v1}(T)$ is the temperature-dependent vacancy density in the matrix (Eq. 25);

 $N_{v2}(T)$ is a second and possibly strong temperature-dependent vacancy density in the matrix;

- N_v(helium internal pressure) is an effective contribution to vacancy density through enlarging the cavity size;
- N_{v2}(cavity shape) is an effective contribution to vacancy density through enlarging the cavity cross-sectional area;

and all other terms are as previously defined.

4. Conclusions and recommendations

4.1 Conclusions

The original development by LLNL of a model for predicting possible lifetime limiting conditions for spent Zircaloy-clad nuclear fuel rods during long-term dry storage occurred in the mid 1980s.¹ This model was adopted as a basis for establishing peak temperature limits during dry storage by the USNRC.^{2,3} The methodology behind the LLNL model was based on a well-known and slowly occurring creep-induced failure mechanism identified as DCCG.⁴⁻⁷

The basic process involved in DCCG is the formation and growth of small cavities on the grain boundaries of a metal subjected to both reasonably high temperatures and a sustained stress loading. The growth aspect of the cavities has traditionally been attributed to the preferential diffusion of vacancies to these cavities as a result of the combined stress-temperature loading.⁴⁻⁷

The DCCG process has been verified for some metals and alloys at conditions consistent with or similar to temperatures and stress conditions seen in spent fuel dry storage environments.^{12,13} Actual evidence that Zircaloy is susceptible to DCCG is very limited;^{8,9} that limited evidence has recently come into question regarding direct applicability to dry storage conditions.¹⁰ However, the DCCG process is still considered a viable candidate for establishing peak temperature limits during dry storage pending the generation of further data that either substantiates or eliminates it as the primary long-term failure mechanism.

The original Zircaloy DCCG modeling¹ involved several assumptions and simplifications that were, of necessity, based on the state-of-the-art knowledge of zirconium and Zircaloy behavior at that time.

Since that model was developed, much new information has become available regarding physical conditions and parameters that govern both general creep behavior and self-diffusion processes in both α -phase zirconium and Zircaloy. However, as was discussed previously, the vast majority of information relevant to improving Zircaloy DCCG modeling comes from the study of pure unirradiated α -phase zirconium or other metals. Also, the zirconium data often is from experiments on a single crystal of α -phase zirconium. Application of this data to irradiated Zircaloy DCCG behavior must always be viewed with skepticism, and be carefully applied considering how the more complex microstructures of the actual irradiated Zircaloy could affect such behavior.

Despite the lack of appropriate irradiated Zircaloy data, the original LLNL-developed Zircaloy DCCG model needed revising. This was necessary to eliminate many of the relatively artificial or data-limited assumptions made in that model. In particular, the assumption of a user-input constant cavity spacing, λ_i , needed an improved physical basis.

With these goals in mind, a two-pronged effort was launched by LLNL to improve the original Zircaloy DCCG modeling. The basic assumptions of the model were challenged from a thermal-physical basis and an extensive literature search was performed to update the physical properties of α -phase zirconium and Zircaloy required by the model.

The former effort has produced a more refined DCCG model that now uses basic α -phase zirconium and Zircaloy material properties to completely define a new thermal-physical basis for describing the DCCG process. Within limits, this new model virtually eliminates the need for user input to fix DCCG parameters for any cause except for inserting improved data. This improved model was discussed in detail in Section 2.1 of this report. However, as discussed there and in Section 3, the updated model is incomplete because it depends solely on the thermal generation of the required vacancy source, N_v(T) (the vacancy density in the grain matrix, Eq. 25), to represent the total vacancy source N_{VTotal}. Whereas, it is expected that N_{VTotal} is a much more complex function (Eqs. 27 and 58) as is indicated from DCCG behavior in other metals.^{12,13}

The latter effort, reported in Section 2.2, has produced an improved basis for selecting such required parameters as values for the grain boundary diffusion coefficient and activation energy. At the same time, newly introduced parameters in the revised model, such as the predominant vacancy formation energy (ΔE_v), required justifiable bases which extended the literature search into new areas.

It is the authors' opinion that the revised DCCG model described in this report has the potential for substantially improving both the understanding of and the ability to model DCCG processes. However, at the same time, it has become obvious through application of this revised model that the model now is ahead of the required data base that would permit the refinement of DCCG modeling as applied to predicting lifetime limiting conditions for spent Zircaloy-clad nuclear fuel rods during long-term dry storage. In particular, more information is required regarding material properties as affected by both fundamental and subtle differences among test specimens of unirradiated α -phase zirconium and Zircaloy and irradiated Zircaloy.

4.2 Recommendations

A primary result of the development and application of the upgraded DCCG model described in this report is the recognition that there is a need for additional work.

- (1) For the present, the updated DCCG model cannot be used as a replacement for the original DCCG model, because, in its current form (current state of irradiated Zircaloy characterization) it cannot completely characterize DCCG cavity growth. Therefore, it is recommended that the original DCCG model be retained. However, it is believed that the original DCCG model is overly conservative; notable gain in permitted long-term dry storage may be possible.
- (2) There is a need to improve the updated DCCG model to incorporate a more complex approach for determining cavity growth. This is particularly true in the area of calculating the cavity-growth source term, the vacancy density in the grain matrix, N_v(T). In addition to being affected by the temperature (Eq. 25), the vacancy density should also be affected by the actual physical characteristics of irradiated Zircaloy. In addition, there may be more complex stress and temperature effects than are currently in the model, as hypothesized in Eqs. 27 and 58.
- (3) There is a need revisit and modify, if needed, some of the basic assumptions of DCCG cavity growth related to the possible presence of non-condensable gas in the cavity and the shape of a growing cavity;
- (4) There is a need for post-irradiation examination efforts that focus on understanding:
 - a) the inter- and intra-grain characteristics of irradiated Zircaloy regarding the presence (density of) or absence of vacancy sites within the grains and cavities on the grain boundaries at the completion of irradiation. This focus should include paired sets of cladding samples where one of each set is additionally aged for a short period at initial dry storage temperature and stress conditions (to see if predicted initial DCCG conditions do occur);
 - b) the same vacancy and cavity density characteristics plus the creep-related behavior of actual spent Zircaloy-clad nuclear fuel rods that already have experienced a long period of both cooldown in spent fuel storage pools and post-irradiation dry storage.

Additional post-irradiation examination efforts could be carried out using well-characterized Zircaloy cladding samples from the program, "Characterization of Spent Fuel Approved Testing

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4. Conclusions and Recommendations

Material."^{19,39-42} Selection of cladding specimens from this program (that already have a welldetailed pedigree) could be a cost-effective method for performing a wide variety of DCCG characterizations and accelerated creep testing. These tests and examinations could be directed to answer not only some of the concerns expressed in this report but other issues that would lead to a better understanding of the likelihood that spent Zircaloy-clad nuclear fuel rods may have lifelimiting characteristics that must be addressed.

References

- 1. M. W. Schwartz and M. C. Witte; <u>Spent Fuel Cladding Integrity During Dry Storage</u>; Lawrence Livermore National Laboratory; UCID-21181 (September 1987).
- "Acceptance as a Reference of Topical Safety Analysis Report for the Castor V/21 Cask Independent Spent Fuel Storage Installation (Dry Storage), Revision 1"; Nuclear Regulatory Commission Report Project M-37 (September 30, 1985).
- "Acceptance as a Reference of Topical Safety Analysis Report for the Westinghouse MC-10 Cask for an Independent Spent Fuel Storage Installation (Dry Storage), Revision 1"; Nuclear Regulatory Commission Report Project M-41 (September 20, 1987).
- 4. D. Hull and D. E. Rimmer; "The Growth of Grain-boundary Voids Under Stress"; <u>Phil.</u> <u>Mag.</u> 4, 673 (1959)
- 5. M. V. Speight and J. E. Harris; "The Kinetics of Stress-induced Growth of Grain-boundary Voids"; Metal Science Journal Vol. 1, pp. 83-85 (1967).
- 6. R. Raj and M. F. Ashby; "Intergranular Fracture at Elevated Temperature"; Acta Metallurgica Vol 23, pp. 653-667 (1975).
- 7. H. Riedel; <u>Fracture at High Temperature</u>, Springer-Verlag Berlin, Heidelberg, Germany (1987).
- 8. R. L. Keussian et al.; "Creep Damage in Zircaloy-4 at LWR Temperatures", Letter to the Editors; Journal of Nuclear Materials Vol. 80, pp. 390-393 (1979).
- 9. R. L. Keussian; <u>Grain Boundary Sliding and Related Phenomena</u>, Ph.D. Dissertation; Cornell University (1985).
- <u>ASTM Manual on Zirconium and Hafnium. ASTM Special Technical Publication 639</u>; J.
 H. Schemel; American Society for Testing and Materials; Philadelphia, Pa. 19103.
- <u>Temperature Limit Determination for the Inert Dry Storage of Spent Nuclear Fuel</u>; EPRI TR-103949 (May 1994).
- 12. R. Raj; "Intergranular Fracture in Bicrystals"; Acta Metallurgica Vol. 26, pp. 341-349 (1978).

- K. Iijima, et al.; "Creep Cavity Growth in Cr-Mo-V Forged Steel for Steam Turbine Rotor"; <u>Creep: Characterization, Damage and Life Assessments</u>; ASM International, pp. 281-286 (May 1992).
- B. A. Chin, et al.; Deformation and Fracture Map Methodology for Predicting Cladding Behavior During Dry Storage; PNL-5998, Pacific Northwest Laboratory, Richland, Washington (April 1989).
- B. A. Chin, et al.; "Prediction of Maximum Allowable Temperatures for Dry Storage of Zircaloy-clad Spent Fuel in Inert Atmosphere"; Nuclear Applications Vol. 85, pp. 57-65 (April 1989).
- H. J. Romeiser and E. Steinberg; Anwendungsorientierte Hullrohrstudie; BMFT-FB K 79-08; BFT; Bonn, Germany (June 1985).
- M. Mayuzmi and T. Onchi; "The Applicability of the Strain-hardening Rule to the Creep Deformation of Zircaloy Fuel Cladding under Dry Storage Conditions"; Journal of Nuclear Materials 178, pp. 73-79 (1991).
- M. Mayuzmi and T. Onchi; "A Method To Evaluate the Maximum Allowable Temperature of Spent Fuel in Dry Storage During a Postulated Accident"; Nuclear Applications Vol. 93, pp. 382-388 (March 1991).
- 19. <u>Characterization of Spent Fuel Approved Testing Material—ATM-104</u>; PNL-5109-104 Pacific Northwest Laboratory, Richland, Washington (December 1991).
- 20. The Mechanical Properties of Matter; Cottrell.
- 21. I. Ursu; <u>Physics and Technology of Nuclear Materials</u>; Pergamon Press, Oxford, England (1985).
- K. Vieregge and Chr. Herzig; "Grain Boundary Diffusion in α-zirconium Part I: Self Diffusion;" Journal of Nuclear Materials 173, pp. 118-129 (1990).
- 23. B. R. Lawn and T. R. Wilshaw; Fracture of Brittle Solids; Cambridge University Press Fracture of Brittle Solids; Cambridge University Press

- 25. Hultgren, et al.; <u>Selected Values of Thermodynamic Properties of Metals and Alloys</u>, John Wiley & Sons, Inc. (1963).
- <u>SCDAP/RELAP5/MOD2 CODE Manual, Volume 4: MATPRO—A Library of Material</u> <u>Properties for Light-Water-Reactor Accident Analysis;</u> NUREG/CR-5273, Vol. IV (February 1990)
- 27. <u>Handbook of Tables for Applied Engineering Science. 2nd Edition</u>, CRC Press, Boca Raton, Fl (1973).
- 28. J. W. Christian; <u>The Theory of Transformations in Metals and Alloys</u>, Section 45; Pergamon Press (1965).
- J. Horvath et al.; "Anomalous Self Diffusion in a Single Crystal of α-zirconium;" Journal of Nuclear Materials 126, pp. 206-214 (1984).
- E. F. de Svarch and C. Rodriguez; "On the Influence of Iron on the Zr-α Self Diffusion;" Journal of Nuclear Materials 185, pp. 167-173 (1991).
- G. M. Hood; "Diffusion and Vacancy Properties of α-Zr "; Journal of Nuclear Materials 139, pp. 179-184 (1986).
- 32. A. M. Garde et al; Acta Metallurgica Vol. 26, p. 152 (1978).
- 33. Dymet and Libanati.
- 34. Suzuoka.
- G. M. Hood; "Solute Diffusion in α-Zr"; Journal of Nuclear Materials 159, pp. 149-175 (1988).
- 36. Thompson.
- 37. J. Takamura; "Point Defects"; <u>Physical Metallurgy</u>, Revised Edition; Edited by R. W. Cahn; North-Eoi¹ end Publishing Company (1970).
- 38. C. P. Flyn <u>selects and Diffusion</u>: University of Illinois, Urbana, Illinois; Clarendon Press Oxford

- <u>Characterization of LWR Spent Fuel MCC-Approved Testing Material—ATM-101</u>, Revision 1; PNL-5109-101 Pacific Northwest Laboratory, Richland, Washington (June 1985).
- 40. <u>Characterization of Spent Fuel Approved Testing Material—ATM-103</u>; PNL-5109-103 Pacific Northwest Laboratory, Richland, Washington (April 1988).
- 41. <u>Characterization of Spent Fuel Approved Testing Material—ATM-105</u>; PNL-5109-105 Pacific Northwest Laboratory, Richland, Washington (December 1991).
- 42. <u>Characterization of Spent Fuel Approved Testing Material—ATM-106</u>; PNL-5109-106 Pacific Northwest Laboratory, Richland, Washington (October 1988).