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SEMI-EMPIRICAL MODELING OF IRRADIATION-INDUCED DIMENSIONAL CHANGE IN H-451 NUCLEAR GRAPHITE

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ABSTRACT

Nuclear graphite has been used as a moderator material in nuclear reactor designs dating back to the first reactor to reach criticality, Chicago Pile 1, in 1942. In addition, it is anticipated to be used in the conceptual Generation four (GenIV) Molten-salt reactors (MSRs) and the High-temperature gas-cooled reactors (HTRs). The macroscopic dimensional change observed in irradiated nuclear graphite is a property change of significant importance. Largely, volumetric change provides valuable insight into the in-service lifetime of graphite components used in nuclear reactors. The dimensional change behavior varies amongst each grade of nuclear graphite due to processing techniques and the resulting microstructure. In this work, historic data for nuclear graphite H-451 is revisited. A semi-empirical methodology is proposed to describe the dimensional change behavior as a function of temperature for nuclear graphite H-451. The turnaround dose, or when there is a reversal of the dimensional change from contraction to expansion, is proposed to be a thermally activated process and thus can be described by an Arrhenius model. On the atomic scale, H-451 is sp^2-bonded carbon atoms with some degree of disorder regardless of orientation. Towards that end, the activation energy is assumed to be a constant irrespective of orientation.

Keywords: Ageing, Elevated Temperature Analysis and Design, Nonmetals, Reactor/Nuclear.

NOMENCLATURE

AG	Against grain
ASME	American Society of Mechanical Engineers
GenIV	Generation four
HOPG	Highly ordered pyrolytic graphite
HTRs	High-temperature reactors
IAEA	International Atomic Energy Agency
MSRs	Molten salt reactors
TAD	Turnaround dose
WG	With grain
A	Pre-exponential
A_x	Anisotropy factor
E_a	Activation energy
F_x	Porosity term
k_B	Boltzmann constant
L	Linear dimensional change
T	Temperature
V	Volumetric dimensional change
γ	Fast neutron fluence
x	Direction (not specific)

1. INTRODUCTION

Irradiation-induced dimensional change is a fundamental response of nuclear graphites. For many high-temperature reactors (HTRs) designs, dimensional change of the graphite is the limiting factor of in-service lifetimes. Upon the onset of irradiation, observed is a net decrease volumetrically. Crystallites of graphite will undergo *c*-axis expansion and *a*-axis contraction during fast-neutron bombardment. Growth of the crystallites is accommodated by porosity within the microstructure. With continuous irradiation, the accommodating porosity densifies, and a reversal of dimensional change occurs, otherwise known as the turnaround dose (TAD). At TAD, significant microstructural changes to the graphite have occurred. Other material properties, such as tensile strength and elastic modulus, will also change significantly at TAD.

While all nuclear graphites show similar behavior when undergoing neutron bombardment, each grade has its own unique response to irradiation due to processing. These processing parameters include, but are not limited to, coke and binder source, filler particle size, graphitization temperature, and billet forming method. Because such variability exists amongst graphite grades, universal models to explain irradiation-induced property change do not exist. Empirical and semi-empirical models are grade-exclusive. Thus, the irradiation behavior code rules for the American Society of Mechanical Engineers (ASME) remain insufficient.

Semi-empirical models to describe dimensional change behavior stem from the seminal work of B.T. Kelley [1–3]. Proposed was that dimensional change in polycrystalline graphites could be expressed as a function of crystallite expansion along the *a* and *c*-axis, an anisotropy factor, porosity, and fast neutron fluence:

$$L_x(\gamma) = A_x L_c(\gamma) + (1 - A_x) L_a(\gamma) + F_x(\gamma) \quad (1)$$

x: Direction (not specific)
γ: Fast neutron fluence (10^{26} n/m^2, E > 0.1 MeV)
L_x: Fractional dimensional change of bulk graphite
A_x: Anisotropy factor
L_c: Fractional dimensional change of *c*-axis direction in a graphite grain
L_a: Fractional dimensional change of *a*-axis direction in a graphite grain
F_x: Porosity term

Highly oriented pyrolytic graphite (HOPG) is shown to have a linear dimensional change behavior due to irradiation [1]. Porosity is believed to decrease up until TAD and then increase with continuous irradiation [4,5]. Therefore, the porosity term has been proposed by others to be a second-order polynomial [6,7], and equation (1) can be expressed as:

$$L_x(\gamma) = a_1\gamma + a_2\gamma^2 \quad (2)$$

where a_1 and a_2 are temperature-dependent constants.

Other semi-empirical models for dimensional change include work by Bradford et al., who proposed a more robust model with a distribution function to describe porosity and interconnectivity and an exponential function to describe dimensional strain [8]. Additionally, a report from General Atomics gives a semi-empirical model for dimensional change of H-451 graphite with astonishing 18 polynomial coefficients for axial and radial directions out to five significant figures [9]. More recently, Srinivasan has proposed a model that uses a fourth-degree polynomial [10]. For any of the models mentioned above, TAD may be calculated by setting the derivative of the dimensional change model to zero:

$$\frac{dL_x(\gamma)}{d\gamma} = 0 \quad (3)$$

All of the aforementioned models describe the amount of dimensional change semi-empirically for a given temperature. Although the TAD is a strong function of temperature, as irradiation temperature increases, TAD decreases [9,11–14]. A temperature-dependent mechanism may be described as Arrhenius behavior. Thus, assuming common activation energy and pre-exponential dependent on macroscale properties, TAD can be expressed as a function of temperature.

2. MATERIALS AND METHODS

In this work, historical data on nuclear graphite H-451 is revisited with a newly proposed Arrhenius model to predict the turnaround dose as a function of temperature. Great Lakes Carbon Company produced H-451 for use as a fuel element graphite [15]. H-451 was extrusion molded and manufactured from petroleum coke, coal tar-pitch binder, and a petroleum pitch as an impregnant [15]. While H-451 is no longer produced, the irradiation data should not be considered obsolete; modern synthetic graphites share some baseline properties and processing techniques.

In the Graphite Design Handbook, General Atomics suggested that H-451 irradiation-induced strain (axial and radial) could be represented as a function of neutron fluence (E>0.18 MeV), temperature, and 18 polynomial coefficients. However, if one assumes temperature to be constant, the model collapses to a third-order polynomial with temperature-dependent coefficients:

$$\frac{\Delta L_x(\gamma)}{L_o} = a_1\gamma + a_2\gamma^2 + a_3\gamma^3 \quad (4)$$

where $\Delta L_x/L_o$ is the dimension strain in a non-specified direction (x) with the coefficients being temperature and directional dependent, as shown in Table 1. Note that the coefficients are rounded to two significant figures in Table 1; however, all significant figures were used to produce plots in this work.

TABLE 1
TEMPERATURE DEPENDANT COEFFICIENTS FOR THE AXIAL AND RADIAL DIRECTIONS, BETWEEN 400-800°C.

		400°C	500°C	600°C	700°C	800°C
a_1	radial	-0.18	-0.14	-5.8E-02	3.0E-02	9.1E-02
	axial	-0.24	-0.18	-7.5E-02	2.4E-02	8.2E-02
a_2	radial	3.1E-03	1.3E-03	-1.4E-02	-4.1E-02	-7.1E-02
	axial	4.0E-03	1.2E-03	-1.6E-02	-4.8E-02	-8.6E-02
a_3	radial	3.5E-05	8.1E-05	7.9E-04	2.7E-03	5.7E-03
	axial	1.9E-05	4.3E-06	6.2E-04	2.6E-03	4.9E-03

The TAD for the theoretical model was calculated by taking the derivative of $\Delta L_x/L_o$ equations in hundred-degree increments from 400-800°C for both radial and axial directions (equation (3)). TAD data points were then plotted as dose vs. temperature and fit with an Arrhenius function (equation (4)).

$$\mathrm{TAD}(T) = A\, e^{\frac{-E_a}{k_B T}} \quad (4)$$

Where:
A: Pre-exponential factor
E_a: Activation energy
k_B: Boltzmann constant
T: Temperature

During the first fitting, the activation energy and pre-exponential were allowed to vary. A second fitting was conducted by setting the activation energy as an average from

axial and radial data, and the pre-exponential was allowed to vary.

3. RESULTS AND DISCUSSION

Figure 1 shows the modeled dimensional strain for H-451 in the axial and radial directions. In figure 1 (b), the model appears to be incorrect at 500°C (red curve) as the amount of dimensional change deviates from the other models and is not observed irradiation behavior [10,12,16]. Furthermore, using equation (3) gives a TAD of approximately 110 dpa, which is wildly incorrect. For these reasons, data for 500°C was excluded from the analysis. It should be noted that the dimensional strain model was said to be valid between 350-1300°C, up to a fluence of 10 x 10^{25} n/m^2 or approximately 8.9 dpa [9]. 8.9 dpa is the precise location in figure 1 where the model for 500°C deviates. Additionally, for temperatures above 800°C, the dimensional change asymptotically approaches +∞ at low fluences.

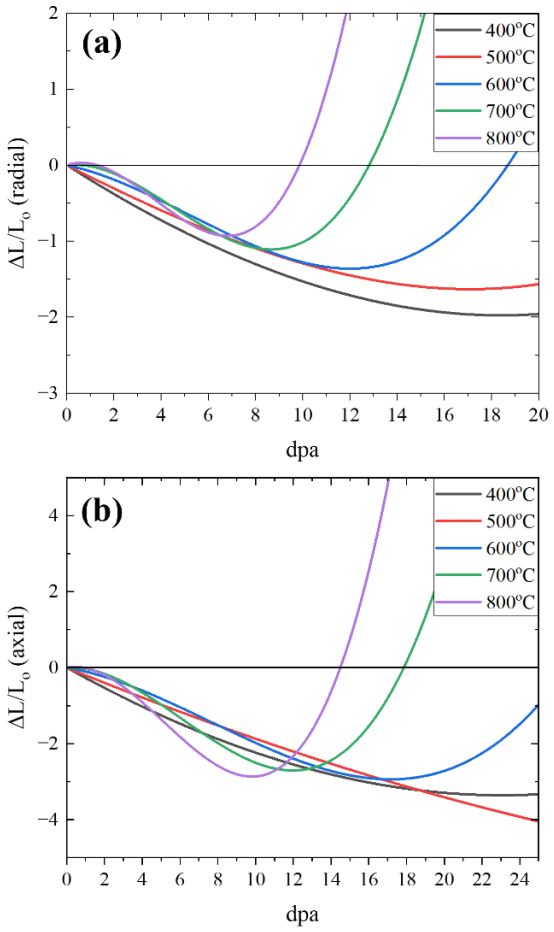

FIGURE 1: MODELED DIMENSIONAL CHANGE FOR H-451 RADIAL (a) AND AXIAL (b) DIRECTIONS.

Another potential reason for the error in the model at 500°C is the lack of data used to develop the model at that time. Figure 2 shows the reported data points for irradiations conducted between 600-700°C, and between 700-800°C [17]. The lowest irradiations temperature was 605°C, and the methodology used to extrapolate design models at 400 & 500°C is not discussed in the references [9,17]. However, excluding data at 500°C, between 400-800°C, the authors argue the model adequately describes dimension change up to TAD [10,12,16].

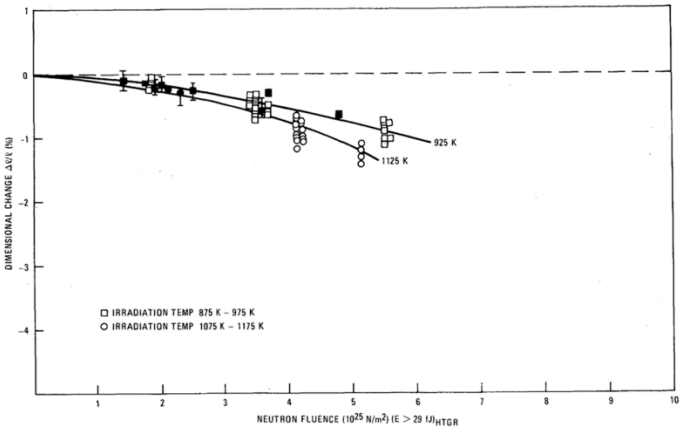

FIGURE 2: DIMENSIONAL CHANGE DATA FOR IRRADIATED H-451 NUCLEAR GRAPHITE. ADAPTED FROM REF. [17].

The TAD was calculated from the dimensional change curves shown in figure 1 using equation (3). Figure 3 shows TAD vs. temperature for both the axial and radial directions. The authors have included assumed error bars to emphasize that there will be an inherent error in temperature and dose during actual irradiation conditions. The vertical error bars presume a five percent error dose calculation, and the horizontal error bars infer a ±25°C in temperature. The data shown in figure 2 was fit using equation (4). Both the activation energy and pre-exponential were allowed to vary for the fitting.

The Arrhenius fits in figure 3 calculate activation energies of -0.14718 eV and -0.1245 eV in the radial and axial directions, respectively. Assuming the mechanism(s) which govern dimensional change behavior occurs on the atomistic scale and not on the macro or mesoscale, the activation energies should be the same as it is the same nuclear graphite. Averaging the activation energies yields a value of -0.13584 eV; this value was held constant during the re-fitting of TAD data, and only the pre-exponential was allowed to vary. The pre-exponential should be a constant representing the macroscale intrinsic properties of the graphite, in this case, orientation.

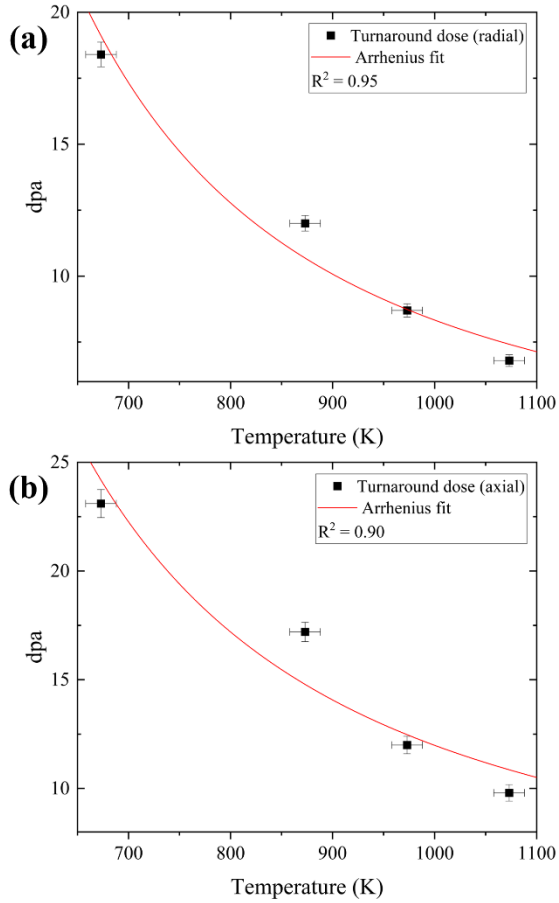

FIGURE 3: ARRHENIUS FITS FOR TAD, ALLOWING THE PRE-EXPONENTIAL AND ACTIVATION ENERGY TO VARY FOR THE RADIAL (a) AND AXIAL (b) DIRECTIONS.

Table 2 shows the results from all Arrhenius fits. In fit 2, despite constraining only the pre-exponential to vary, the R^2 values remain reasonable and indicate the goodness of fit. The orientation of the graphite component is directly related to a preferential grain orientation due to the extrusion forming during manufacturing. Extrusion and the earth's gravitational field give rise to the lenticular filler particles preferentially lying flat along the axial direction. Therefore, the axial and radial directions can be referred to as with grain (WG) and against grain (AG), respectively.

TABLE 2
KEY FITTING PARAMETERS FOR BOTH ARRHENIUS FITS. IN FIT 2, E_a IS HELD CONSTANT, AND ONLY A IS ALLOWED TO VARY.

Fit 1	E_a (eV)	A	R^2
Radial	-0.14718	1.51019	0.94905
Axial	-0.12450	2.82612	0.89573
Fit 2	E_a (eV)	A	R^2
Radial	-0.13584	1.76139	0.94137
Axial	-0.13584	2.41341	0.88618

Figure 4 shows both Arrhenius functions from fit 2. The axial direction corresponds to a higher A value and a sooner TAD. In comparison, the opposite is true for the radial direction. As shown in figure 3, such plots may be valuable for reactor design. In many instances, graphite components will experience a gradient in temperature and neutron flux in the reactor. As such, it may be advantageous to have components cut with respect to a particular orientation of the graphite billets, accommodating the respective linear dimensional changes to the gradients in temperature and neutron flux.

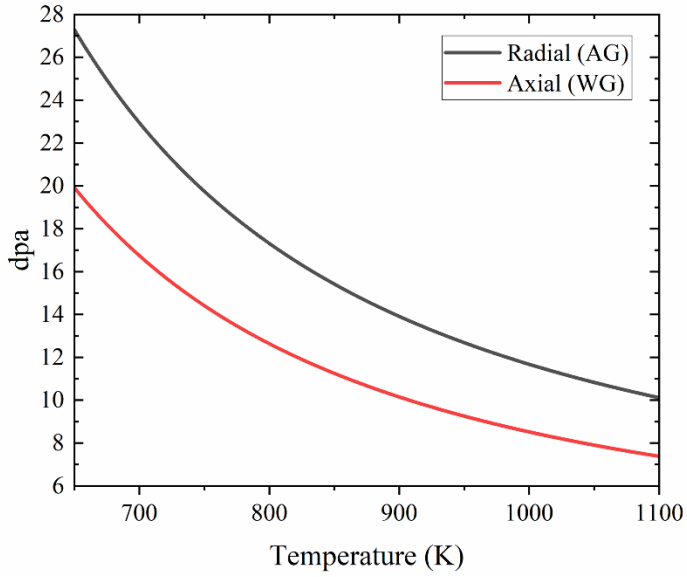

FIGURE 4: ARRHENIUS FITS FOR TAD FOR RADIAL (IN BLACK) AND AXIAL (IN RED) DIRECTIONS.

The aforementioned methodology may indeed be advantageous for a specific grade of nuclear graphite when considering reactor design; however, it requires an extensive amount of irradiated specimens, which must be conducted over at least three temperature regimes, and produce enough data point well past TAD. Such irradiation campaigns are costly and time-consuming and are not a viable option for the next-generation nuclear graphites desired for reactor designs in the next decade.

Specifically, for ASME code development, the methodology mentioned above is proposed by the authors to be modified for a universal activation energy for all nuclear graphites. The hypothesis is that all nuclear graphites are the same on the atomic level, sp^2 bonded Carbon with some degree of disorder. Thus, the pre-exponential can be used to describe the macroscale properties of a grade of nuclear graphite. These properties include but are not limited to grain size, anisotropy, and density. To normalize the analysis to include all grades of nuclear graphite, as opposed to the linear dimensional change, volumetric dimensional change normalizes the graphite billet's geometry.

The authors are currently compiling all available open-source volumetric change data, including all data available within the International Atomic Energy Agency (IAEA) database [18]. Figure 5 shows historical grade ASR-1RS data from irradiation conducted at 400°C ±6. Nuclear graphite ASR-1RS was produced by the German company Sigri Elektrographit GmbH (later SGL Carbon) and was vibration molded and made from a pitch coke [19]. As outlined in section 1, there is no accepted theoretical model to describe the amount of dimension change to date. Therefore, the authors have chosen to use a purely empirical 5th-order polynomial. The R^2 for the fit in figure 4 is 0.99278.

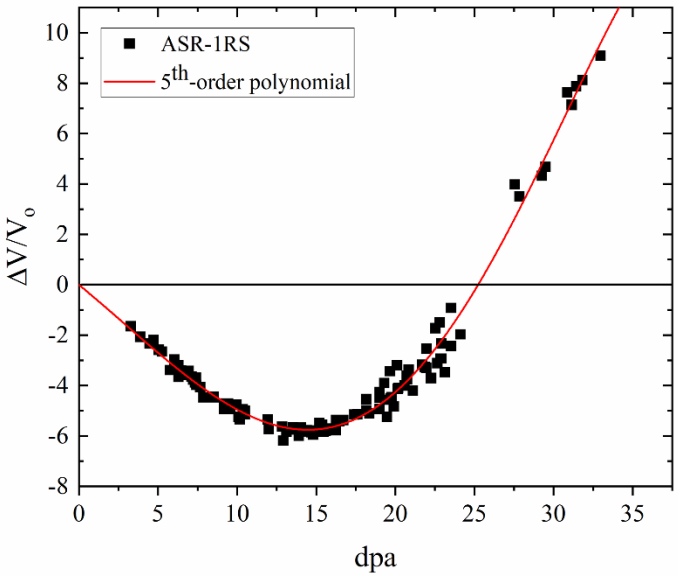

FIGURE 5: DIMENSIONAL CHANGE FROM IRRADIATION CONDUCTED AT 400°C ON NUCLEAR GRAPHITE ASR-1RS.

For nuclear graphite ASR-1RS, irradiation data were analyzed in three temperature regimes, 400, 500, and 600°C. From the best-fit polynomials, the TAD was extrapolated using equation (3). Figure 6 shows the Arrhenius fitting of the volumetric change data for ASR-1RS. The vertical error bars assume a five percent error in dose calculation, and the horizontal error bars represent one standard deviation from the average reported irradiation temperature. The Arrhenius fit is exceptional, with an R^2 value of 0.99995. The activation energy is approximately 0.03 eV from the analysis conducted on the H-451 model, and the pre-exponential is within 0.2 of the highest value.

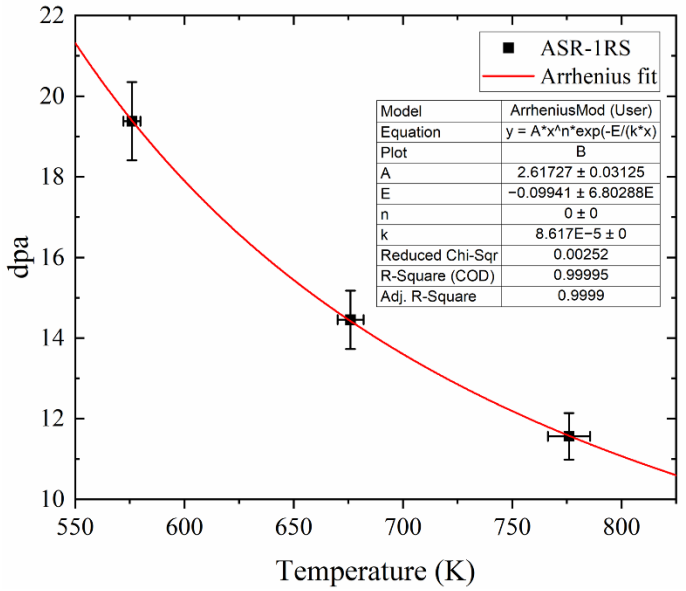

FIGURE 6: ARRHENIUS FIT FOR NUCLEAR GRAPHITE GRADE ASR-1RS.

4. CONCLUSION

Historical models describing the linear dimensional change behavior of nuclear graphite H-451 have been revisited. Proposed is a methodology using an Arrhenius function to determine TAD. This model assumes the activation energy to be a constant for all graphites. This methodology will be extended to volumetric dimensional change of all nuclear graphites. The preliminary volumetric analysis is shown for nuclear graphite ASR-1RS, and the results suggest the method to be sound.

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