Assessment of Annealing Parameter Approximations in Zirconium Alloys

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Abstract
Critical to reliable performance of zirconium alloys is an understanding of the effects of processing and service on properties. To obtain this understanding, extensive experimentation is performed, but the challenge then becomes comparing test data from different conditions and using it in extrapolation. To address this, the annealing parameter (AP) has become a popular metric. Various AP formulations have been proposed, enabling data from different times and temperatures to be directly compared. The AP also allows complex multi-step heat-treatments to be related to an isothermal equivalent. This has proved useful in rationalizing the evolution of second phase particles (SPPs) size in Zircalloys and related properties such as corrosion resistance. Implicit in the annealing parameter approach are assumptions about the mechanism controlling microstructural evolution and its path independence. This work critically evaluates the validity of these assumptions through comparison with well controlled predictions from a physical model for SPP evolution. It is shown that once SPP evolution has entered the coarsening regime, AP approaches are valid, but prior to this they are not. It is demonstrated that for SPP evolution in Ziraloys, coarsening dominated kinetics are established rapidly and thus for most practical cases the AP approach is appropriate.

Keywords: Annealing parameter, Zircaloy, Second phase precipitates, Modelling

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1. Introduction

Zirconium alloys for use in nuclear reactor applications have been developed largely by empirical trial and error methods for over 60 years [1]. During this time, there have been considerable efforts to understand the link between microstructure and performance in service. In many cases, this has led to experimentally derived design criterion to achieve desired performance. For example, corrosion behaviour is optimized by controlled annealing heat treatments to obtain a certain microstructural state [2, 3, 4]. However, there remains a lack of a mechanistic understanding between the microstructure and critical performance parameter.

One of the challenges in obtaining such an understanding is the complex process and exposure conditions typically experienced by a zirconium alloy. For example, the production of fuel cladding involves several stages of deformation and heat treatment. Subsequent service leads to further microstructural evolution involving interactions between thermal and irradiation effects. To understand the performance and ensure the safety of zirconium alloy components, it is usual to carry out a large number of tests across a range of conditions. For example, autoclave exposure across a range of temperatures and times and in a variety of media are typically used to study corrosion behaviour. Sometimes this is accompanied by microstructural studies to identify the apparent feature controlling the corrosion response [3, 4].

In analysing such results it is convenient to be able to directly compare data acquired under different conditions of time and temperature. To relate this to real conditions during processing and service, it is useful to be able to reduce the real complex multi-step thermal treatment to an equivalent isothermal temperature and time. For both purposes, the concept of an “effective” annealing parameter has become popular within the nuclear community [1, 3, 4, 5, 7, 8, 9]. The effective annealing parameter combines time and temperature information into a single variable so that data from material exposed at a range of times and temperatures can be directly compared. The annealing parameter concept also allows complex heat treatments to be reduced to a single numerical value, for which an equivalent isothermal treatment can be found. The utility of this approach has been demonstrated empirically for Zircaloys, with a good correlation found between annealing parameter values and properties such as corrosion resistance, mechanical properties, and creep resistance (e.g. [1, 3, 6, 7]).

The annealing parameter for zirconium alloys was first developed for
Zircaloy-4 in the context of recovery and recrystallization leading to a hardness reduction after cold work [5]. It was demonstrated that hardness changes for different combinations of annealing time and temperature collapsed onto a single line of best fit when plotted as a function of a fitted annealing parameter. The cumulative annealing parameter [5], a revised version referred to as the second order cumulative annealing parameter [10], and the closely related particle growth parameter [1] have since been applied more widely, for example to rationalize corrosion behaviour under different conditions. The validity of this approach has been demonstrated empirically and explained through the good correlation found between annealing parameter and mean SPP size [3] or matrix composition [4] over a range of temperatures.

The first annealing parameter proposed and widely adopted is the cumulative annealing parameter (CAP), defined for a \( n \) step thermal process as [5]

\[
CAP = \sum_{i=1}^{n} t_i \exp \left( \frac{-Q_c}{RT_i} \right)
\]  

(1)

Where \( t_i \) and \( T_i \) are the time and temperature of the \( i \)th thermal step, \( Q_c \) is a fitting parameter (an effective activation energy), and \( R \) is the molar gas constant.

Other similar equations have also been proposed for specific aspects of the microstructure, for example SPP growth. In this case, a particle growth parameter (PGP) was proposed as [1]

\[
PGP = \sum_{i=1}^{n} k t_i \exp \left( \frac{-T_A}{T_i} \right)
\]  

(2)

Where \( k \) and \( T_A \) are fitting parameters. An empirical addition to the PGP was proposed to account for the precipitation that occurs during \( \beta \) quenching in the practically important case where the cooling rate is too slow to prevent quench induced precipitation.

Another version of the annealing parameter was proposed by Gros and Wadier [10]. They attempted to produce a more physically meaningful parameter by appealing to coarsening theory and formulating an expression that directly gives the mean SPP diameter (\( D \)). This approach also allows (in a more physical way) for quench induced precipitation to be considered [10]. They defined their parameter as the SOCAP (second order annealing parameter) since it was based on Kahlweit’s coarsening model that considers second order kinetics [11]. The SOCAP is given by [10]:
SOCAP = D^3 - D_0^3 = \left[ \frac{k_s}{T^2} \exp \left( \frac{-Q_s}{RT} \right) \right] t \quad (3)

Where $D_0$ is the initial particle diameter, and $k_s$ and $Q_s$ are fitting parameters.

Equations 1, 2, 3 have the general form of an Arrhenius equation (or modified Arrhenius equation in the case of the SOCAP), in which $Q$ can be identified as an effective activation energy. This form is justified since recovery, recrystallization, SPP growth, and coarsening are all processes requiring thermal activated atomic movement, which obeys an Arrhenius law [12].

However, as demonstrated later, the useful simplification of collapsing all the physical processes into a single effective activation energy can lead to non-physical results under some conditions. For example, these equations predict that a decrease in temperature will always lead to slower kinetics (longer time to reach the same value of the CAP, PGP, or SOCAP). In the case of diffusion controlled nucleation and growth of SPPs there is a competition between driving force due to supersaturation (higher at lower temperature) and diffusion (faster at higher temperature). This leads to the well known C-curve behaviour for overall kinetics as a function of temperature [12]. Above the nose of the C-curve higher temperatures will lead to slower SPP precipitation kinetics as the reduced driving force for precipitation becomes dominant. This is the opposite of the behaviour predicted by annealing parameter models.

Another implication of these equations is that the microstructural state is path independent; i.e. the order of the process steps does not matter. However, this may not be the case. For example, with respect to SPPs, a low temperature treatment followed by a high temperature treatment can often produce a very different microstructure from that obtained if the order of heat treatments is reversed. This is because the various physical processes (nucleation, growth, coarsening) all have different dependencies on temperature.

It is thus important to determine the range of conditions under which CAP, PGP, and SOCAP approaches are valid with respect to the typical annealing, testing, and service conditions encountered by zirconium alloys. In particular, this paper will address the use of these parameters in making a correlation with SPP size [1] or matrix composition [4]. To provide a consistent and controllable dataset for comparison, a precipitation model has been used to generate simulated PSDs for a range of different single and
multistep heat treatment processes. The model, which has been discussed in detail elsewhere [13, 14], is based on the Kampmann and Wagner Numerical framework [15] in which nucleation, growth, and coarsening processes are all considered and allowed to evolve naturally.

2. Precipitate Evolution Model

The model used in the present work has been described in detail elsewhere [13] and only the essential features will be summarized here. The model is based on classical kinetic theory for nucleation and diffusion controlled growth, and these equations are coupled using Kampmann and Wagner Numerical (KWN) method [15, 14]. The key features of the model are [13]:

1. The full particle size distribution (PSD) is tracked through nucleation, growth, and coarsening and is discretized into a large number of size classes.
2. The continuous time evolution of the particle distribution and matrix solute level is considered in terms of discreet time steps.
3. The complex chemistry of Zircaloy is simplified to a pseudo-binary system, with an effective diffusivity and solute concentration used that accounts for both Fe and Cr, following Massih et al. [16].
4. The number of new particles in each time step is calculated using classical nucleation theory.
5. The exchange of particles between size classes is calculated assuming solute diffusion is the rate limiting process and a spherical growth morphology.
6. The Gibbs Thomson relationship [12] is used to calculate the modified interfacial compositions for each size class and at each time step.
7. The change in matrix solute level due to precipitate formation or dissolution is calculated at each time–step. A mean field approximation is used to track the average matrix solute level to be used in the next time–step.
8. The transition from nucleation to growth and then coarsening dominated kinetics is not imposed but arises naturally in the model due to the continuous change in matrix solute level and its effect on the instantaneous supersaturation.
9. The time–step is incremented and the model is iterated until the end time is reached.
Table 1: Input parameters for the PGP, CAP, SOCAP and KWN kinetic models with source.

| Parameter                                           | Value                                | Source |
|-----------------------------------------------------|--------------------------------------|--------|
| Molar volume $V_m$                                  | $9 \times 10^{-6} \text{m}^3 \text{mol}^{-1}$ | [16]   |
| Solute concentration in particle $c^\beta$          | 54 at.%                              | [16]   |
| Effective nucleation site density                   | $21.5 \times 10^3 \mu\text{m}^{-3}$ | [16]   |
| Effective interfacial energy                        | 0.25 Jm$^{-2}$                       | [16]   |
| Effective activation energy for diffusion            | 132.4 kJmol$^{-1}$                   | [16]   |
| Effective pre-factor for diffusion                   | $1.473 \times 10^{-6} \text{m}^2\text{s}^{-1}$ | [16]   |
| Activation energy for CAP $(Q/R)$                    | $4 \times 10^4 \text{K}$            | [3]    |
| $T_A$ for PGP                                        | $3.2 \times 10^4 \text{K}$          | [1]    |
| $k$ for PGP                                          | $1 \times 10^{14} \text{h}^{-1}$    | [1]    |
| $k$ for SOCAP                                        | $1.11 \times 10^{-11} \text{m}^3\text{s}^{-1}\text{K}^2$ | [10]   |
| Activation energy for SOCAP $(Q/R)$                  | $1.87 \times 10^4 \text{K}$         | [10]   |

The resultant model is capable of predicting nucleation, growth, coarsening without artificial constraints, whether these processes occur concomitantly or sequentially. The model developed here uses a Runge-Kutta scheme to determine the time interval for each step to ensure model efficiency and numerical accuracy, and this is discussed in detail elsewhere [14].

The model relies on a number of input parameters, summarised in Table 1. In particular, there are two parameters that have a large influence on the predictions but that are not known a priori. These are the interfacial energy of the SPPs, and the nucleation site density. Values for these parameters were taken directly from those used in previous work to model SPP formation in Zircaloy–2 [16], which themselves were derived from experiments on Zircaloy–4 [10]. No further tuning of these values was undertaken since the purpose of the present model was not to provide a high level of quantitative accuracy (which would not be justified given the inherent approximations) but rather to enable a physically realistic simulation of SPP evolution under a range of conditions to be compared with expectations from application of annealing parameter approaches. As demonstrated previously [13], these fitting values when used in the present model give a reasonable prediction of the particle size and number density after a simulated annealing treatment.
3. Results and Discussion

To understand the functional forms and compare the CAP, PGP, and SOCAP it is useful to visualize these parameters as a function of time and temperature (for an isothermal heat treatment). Figure 1 shows contour plots of (a) CAP, (b) PGP, and (c) SOCAP as a function of time and temperature. To produce these plots, the values of $Q$, $k$, and $T_A$ taken from the literature were used, as summarized in Table 1. These values are commonly accepted in the literature as appropriate for Zircaloy-2 and 4 [1, 10]. All simulations were performed using a chemical composition corresponding to Zircaloy-4.

![Figure 1: Contour plots showing the calculated values for (a) the cumulative annealing parameter (CAP), (b) particle growth parameter (PGP), and (c) second order cumulative annealing parameter (SOCAP) as a function of time and temperature for isothermal treatment.](image)

As expected, all of these parameters produce a similar trends with respect to time and temperature. Changes in temperature have a much stronger effect than changes in time across the range of practical interest, a consequence of the Arrhenius behaviour. The introduction of a second temperature term in the SOCAP equation gives difference in the relative significance of temperature and time in determining the annealing parameter, changing the gradient of the contour lines in Figure 1(c).

Figure 2 shows the model predictions of mean particle radius for isothermal heat treatments between 903 and 1073 K, plotted as a function of the
originally proposed cumulative annealing parameter (CAP). This temperature range corresponds to that for which SPP size measurements are reported by Garzaroli et al. [3]. In performing the simulations, it is assumed the prior \( \beta \) quench was perfect; i.e. no SPPs formed during the quench, so all the supersaturated solute is available for precipitation.

![Predicted evolution of particle radius for a range of temperatures plotted as a function of the CAP](image)

Figure 2: Predicted evolution of particle radius for a range of temperatures plotted as a function of the CAP for (a) an effective \( Q/R = 40000\, \text{K} \) [3], (b) an optimized \( Q/R = 17000\, \text{K} \) that collapses the predictions onto a single curve in the coarsening regime.

Figure 2(a) is a plotted using the standard \( Q/R \) value derived from experiment by [3]. It can be seen that the particle radius evolution plots are slightly displaced using this value for the activation energy. The shape of these curves is a consequence of a transition in dominant processes during SPP evolution. In the initial period, precipitates are nucleating and growing, and the mean particle radius increases. A plateau region is then reached. At this point, the supersaturated solute has been depleted, nucleation has stopped, and coarsening has begun. Particles smaller than a critical size are shrinking, particles larger than this size are growing, but the smallest particles have not yet disappeared. The growth and shrinking processes lead to an evolution of the PSD but at constant mean size. Eventually, the smallest particles dissolve completely and are removed from the PSD, at which point the mean radius starts to increase. Beyond this time, it has been
demonstrated previously that the KWN model gives a predicted evolution in PSD and mean particle size with temperature that closely matches that expected by classical coarsening theory [15]. The factors that control the relative duration of these regimes for a general case are discussed in detail elsewhere [17].

By adjusting \( Q \) (Figure 2(b)) the size evolution data for \( \text{CAP} > 1 \times 10^{-5} \) s collapse onto a single curve as required for the CAP approach to be valid. This corresponds to the coarsening dominated regime. Classical Lifshitz–Slyozov–Wagner (LSW) coarsening theory gives the evolution of mean particle radius in this regime as [15]:

\[
\bar{r}^3 - \bar{r}_0^3 = \alpha_{LSW} (t - t_1)
\]

where \( t_1 \) is the time at the onset of coarsening. The coarsening parameter, \( \alpha_{LSW} \), is given by

\[
\alpha_{LSW} = \frac{8V_mD\gamma c^\alpha}{9RT(c^\beta - c^\alpha)}
\]

Where \( c^\alpha \) is the equilibrium concentration of solute in the matrix (the solvus boundary without curvature effects), \( D \) is the effective solute diffusion coefficient and other parameters are defined in Table 1. The two significantly temperature dependent terms in this equation are \( D \) and \( c^\alpha \). Both can be written in the form of an Arrhenius equation, with \( Q/R = 2.8 \times 10^3 \) K in the expression for \( c^\alpha \) [16] and \( Q/R = 15.9 \times 10^3 \) K for \( D \) [16]. The activation energy for diffusion thus dominates the overall activation energy (being 5.7 times greater than that defining the solvus boundary). The effective activation energy during the coarsening regime is thus expected to be dominated by the activation energy for diffusion. The optimum activation energy to collapse all the predictions onto a single curve during the coarsening regime (\( Q/R = 17 \times 10^3 \) K) is close to the activation energy for diffusion used in the model. This is considerably lower that the value of \( Q/R = 40 \times 10^3 \) K derived from experimental fitting [3]. This optimised activation energy value is used for all subsequent CAP calculations in this work.

An important observation is that prior to the onset of coarsening, the radius data do not collapse onto a single curve in the CAP plot, even using an optimised value of the effective activation energy. This is because prior to coarsening becoming established, the microstructural evolution is not controlled simply by diffusion, but also by driving force (supersaturation) and
thus there is a more complex relationship with temperature. This is even more apparent when other SPP parameters are plotted, such as number density.

Figure 3 shows predictions for a wider range of temperatures, varying from 673–1073 K (400–800°C). The plot of mean radius against CAP (Figure 3(a)) demonstrates again that once the coarsening dominated regime has been reached, all the data collapse onto a single curve even over a large temperature (and time) range (5h – 1000h).

\[\text{Figure 3: Predicted evolution of mean SPP radius at different temperatures plotted as a function of (a) CAP (Q/R = 17000 K) and (b) time. Predicted evolution of (c) SPP number density and (c) matrix solute level for the same temperatures plotted as a function of CAP.}\]

Figure 3(b) shows the model predicted radius plotted simply as a func-
tion of time. This plot demonstrates the utility of annealing parameter approaches. When the data is plotted in this (raw) form, the curves for each temperature are separated, not simply related, and there is no possibility of easy interpolation or extrapolation to conditions for which there are no data (e.g. to other temperatures or times).

Figure 3(c) shows the predicted particle number density as a function of CAP. In the coarsening regime, the data collapse onto a single curve, but prior to this (CAP < 10^{-6} s) there is a large variation in predicted number density for the same value of the CAP. This demonstrates that whilst the CAP gives a good method of comparing number density and radius data from different temperatures once coarsening has become well established, prior to this the SPP size and number can be very different at different temperatures, even for the same value of CAP.

Finally, Figure 3(d) shows the SPP volume fraction as a function of CAP. Plotting the data as a function of CAP results in a much narrower spread (that if plotted only as a function of time, for example). The terminal volume fraction reached is a function of temperature since this is controlled by the solvus concentration for a given precipitate composition. Over the temperature range of practical interest in the annealing of Zircaloys, the solvus composition changes only slightly, and thus the changes in terminal volume fraction are small.

The PGP and SOCAP equations were proposed as improvements over the original CAP formulation. To determine if there are likely to be any practical differences when using these approaches, mean particle size was also plotted as a function of PGP and SOCAP to compare with plots using the CAP (Figure 4). Figure 4 shows that PGP (unfitted) does not produce a collapse of predictions from different temperatures onto a single curve, but such a collapse could be achieved by tuning the activation energy (not shown). This is to be expected, since the PGP and CAP have the same functional dependence on temperature.

Use of the SOCAP (taking calibration parameters from [10] without refitting) leads to a convergence of the curves from different temperatures as for the fitted CAP plot (Figure 4(a)). This is because the activation energy proposed for the SOCAP model is directly related to the effective activation energy for diffusion, and as demonstrated this is the controlling factor in determining the temperature dependence of the coarsening process. These calculations suggest that there is no particular advantage in using the PGP over the CAP to fit size evolution data during the coarsening regime. Sim-
Figure 4: Predicted evolution of mean SPP radius at different temperatures plotted as a function of (a) CAP (fitted, $Q/R = 17000$ K), PGP (not fitted) [1], SOCAP (not fitted) [10].

Similarly, whilst the SOCAP has a stronger physical basis than the CAP, in practical application it provides a no better fit to the results in the coarsening regime, and suffers from the same problems as the CAP prior to the onset of coarsening (i.e. divergence of the data at different temperatures).

It has been argued that rather than correlating with the SPP size, the corrosion behaviour in Zircaloys better correlates with the concentration of solute remaining in the matrix [4]. Figure 5 show the predicted evolution of solute in the matrix (which is the inverse of the volume fraction of SPPs). As already discussed, the model is based on considering an effective solute concentration, which considers the effects of both Fe and Cr, as used by Massih and Jernkvist [16].

The solute decreases most rapidly during the early nucleation and growth stage of the transformation where the SPP volume fraction is strongly increasing. Plotting the data against time (Figure 5(a)) gives a series of curves with a large difference in the time range over which the solute level drops, from fractions of a second at 1073 K to over 1 h at 903 K.

If the same data are plotted as a function of CAP or SOCAP, then as Figure 5(b) and (c) show, the curves from different temperatures converge, so that the period in which the solute drops rapidly falls within a narrow range of CAP or SOCAP values. This demonstrates the usefulness of these parameters in comparing data from different temperatures and interpolating to new temperatures, even if the controlling mechanism of interest is the solute concentration in the matrix. Again, from a practical perspective, there is no
Figure 5: Predicted evolution of solute in the matrix at different temperatures plotted as a function of (a) time (b) CAP (fitted, $Q/R = 17000$ K), (c) SOCAP (not fitted) [10].

advantage to using the SOCAP calculation over the CAP for this purpose. Since the rapid drop in solute concentration in the matrix occurs earlier in the precipitation sequence than coarsening, the critical CAP or SOCAP values when the solute in the matrix changes rapidly are around 2–3 orders of magnitude less than the CAP or SOCAP values at which coarsening becomes dominant. Therefore, the specific CAP or SOCAP value that correlates with a change in behaviour (e.g. corrosion rate) will be lower if the controlling mechanism is change in matrix solute level rather than increase of SPP size by coarsening.

The KWN model also predicts the complete particle size distribution (PSD) as well as averaged parameters. It is interesting to compare the predicted PSDs for conditions that produce the same CAP, and examples of such a calculation is shown in Figure 6. Figure 6(a) shows predicted PSDs for a CAP of $10^{-7}$ s at 673 and 1073 K (400 and 800°C), a condition prior to the pure coarsening regime. As shown, for this condition, the same CAP will not correspond to the same PSD. Not only are the mean size and number density different, but so is the shape of the PSD. This is because the balance of nucleation and growth change as a function of temperatures and the PSD is at a different stage of its evolution in these two cases. Figure 6(b) shows predicted PSDs for a CAP of $10^{-4}$ s, which corresponds to early in the coarsening regime. The PSDs converge, but again there are some differences in the shape. The higher temperature PSD is closer to the expected log-normal distribution for LSW coarsening than that at lower temperature. This demonstrates that even at larger values of the CAP, where the mean
particle size values are close, there can remain a difference in the shape of the PSD, which may be practically significant.

![Figure 6: Predicted SPP size distributions at compared at 673 and 1073 K and the same CAP value for (a) low CAP (nucleation and growth regime) (b) high CAP (coarsening regime).](image)

The results presented so far demonstrate the use of the CAP, PGP, and SOCAP to compare data from different temperatures is justified once coarsening has become the dominant mechanism of SPP evolution. The time that this condition is reached is dependent on the temperature, being shorter as temperature increases. A prediction of the critical time for pure coarsening to become established as a function of temperature is shown in Figure 7. This time is clearly a very strong function of temperature, predicted to be only 3 s at 1073 K but over 430 h at 673 K.

The CAP, PGP, and SOCAP approaches are not limited to isothermal treatments, but can also be applied to the more complex non-isothermal and multi-step treatments experienced in industrial processing. This has the great potential advantage of enabling these complex heat treatments to be reduced to an equivalent isothermal treatment that produces the same CAP, PGP, or SOCAP value. Providing there is a direct 1-to-1 relationship between the CAP, PGP and SOCAP and the microstructural parameter of interest, this enables data from isothermal testing (e.g. corrosion data) to be directly used to predict performance for a complex industrial heat treat-
Figure 7: Predicted transition from nucleation and growth to coarsening dominated SPP evolution for isothermal treatment as a function of time and temperature.
ment. However, the range of conditions for which this approach is likely to be reasonable has not been determined. In particular, as discussed in the introduction, there are situations where path effects can be very important and the isothermal equivalent concept will not be valid. Blind application of the CAP, PGP, or SOCAP methods in such situations will lead to invalid results, which could be misleading if applied in the design process.

To investigate this, the KWN model was run for a number of possible scenarios of interest including slow $\beta$–quenching, multi-stage annealing, 2-step thermal exposure at different temperatures, and slow cooling/heating. The results have been compared with predictions for an isothermal equivalent treatment at 673 K (400°C), a popular temperature for autoclave testing. The PGP approach is omitted for brevity, since as already demonstrated, it is functionally equivalent to the CAP method.

A heat treatment in the $\beta$ phase field followed by a quench is used in the manufacture of Zircaloy components. The quench rate will be slower at the billet center than surface, and at the centre it is usually impossible to prevent quench induced precipitation of SPPs. Even for small test specimens (e.g. 25 mm diameter), quenched into water, cooling at the center is sufficiently slow to allow copious SPP precipitation [16]. Using cooling data from [16], the KWN model was applied to predict precipitation during $\beta$ quenching at the center of a 25 mm diameter billet. This scenario was also simulated by the model developed by Massih and Jernkvist [16]. The evolution of the CAP and SOCAP parameters were calculated during the $\beta$ quench.

Figure 8 shows the predicted evolution of mean particle radius, number density, and solute remaining in matrix for a $\beta$ quenching from 1323 K at a rate of 90° s$^{-1}$, a linear approximation to the temperature profile reported in [16]. Figure 8(d) shows the predicted PSD at the end of the quench and Figures 8(e) and (f) show the evolution of the CAP and SOCAP during the quench respectively. The mean SPP radius at the end of the quench is predicted to be 16 nm, which is in reasonable agreement with that predicted by the Massih and Jernkvist model (14 nm) [16]. The model predicts that most of the solute is precipitated during the $\beta$ quench. The predicted PSD is close to the log-normal form that becomes established during the later stages of precipitation and coarsening. The CAP and SOCAP values at the end of $\beta$ quenching correspond to an advanced stage of SPP evolution (e.g. by comparison to Figures 4 and 5).

In the manufacture of Zircaloy cladding, $\beta$ quenching is followed by multiple metal working stages with intermediate annealing heat treatments. The
Figure 8: Predicted evolution of SPP parameters during $\beta$ quenching at 90° s$^{-1}$ (a) SPP mean radius, (b) number density (c) solute in matrix. (d) Predicted SPP size distribution after $\beta$ quenching. Evolution of (d) CAP and (e) SOCAP for the same $\beta$ quenching.
CAP or SOCAP are commonly applied to determine the cumulative effect of these annealing steps on SPP distribution or matrix composition. It is assumed that deformation during the working processes does not influence these microstructural parameters [3]. The KWN model was run for the situation considered by Massih and Jernkvist [16], namely a β quench (as already described) followed by two annealing steps at 838 K for 1h and 1.5h respectively, with a cooling and heating cycle between each step. The thermal profile and results from the simulation are shown in Figure 9. The KWN model predicts the further evolution of the SPPs during the anneals, and these predictions are similar to those reported by Massih and Jernkvist [16]. The SPP evolution during annealing is dominated by coarsening. The predicted PSD approaches the expected log–normal form for LSW coarsening, and the matrix solute level is predicted to slowly fall continuously during the annealing steps. The CAP and SOCAP values at the end of the annealing steps fall within the coarsening regime (e.g. by comparison to Figures 4 and 5).

As already discussed, the CAP and SOCAP methods are path independent and therefore will be unable to predict the effect that path differences may have on SPP evolution. To investigate this for an example situation, KWN simulations were performed for the case of a two stage treatment consisting of a high temperature step (973 K) and a low temperature step (623 K) with a 10s heating or cooling time between steps. Both high–low and low–high combinations were considered, and the predicted evolution of particle radius and matrix solute level are shown in Figure 10 and 11 respectively.

It can be seen (Figure 10) that although the predicted SPP radius evolution follows a different pathway depending on the order of the steps, the final predicted radius reached is the same in both cases (50 nm). In both cases, the SPP evolution is well into the coarsening dominated regime at the end of the thermal steps. This demonstrates that with regard to SPP radius, the order of process steps is not critical once the SPP evolution is sufficiently advanced in the final step to be in the coarsening regime, and in this case the assumption of path independence in the CAP or SOCAP methods is reasonable. However, in regard to matrix solute level (Figure 11) the final concentration does depend on the path. This is because the solubility is a function of temperature, and when the second step is at higher temperature (973 K) the final (near equilibrium) solute level is higher. However, as previously mentioned, over the range of temperatures of commercial interest, the change in solubility is relatively small (compared to the total alloying
Figure 9: Predicted SPP evolution for a $\beta$ quench and two step anneal at 838 K (a) SPP mean radius, (b) number density (c) solute in matrix. (d) Predicted SPP size distribution at the end of treatment. Evolution of (d) CAP and (e) SOCAP for the same thermal process.
element concentration) and therefore the CAP or SOCAP methods may still be reasonable.

Figure 10: Predicted evolution of mean SPP radius for a two stage treatment consisting of (a) high temperature–low temperature (973–623 K) steps, (b) low temperature–high temperature (623–973 K) steps.
Figure 11: Predicted evolution of solute in matrix for a two stage treatment consisting of (a) high temperature–low temperature (973–623 K) steps, (b) low temperature–high temperature (623–973 K) steps.
The final example considered is continuous cooling compared with continuous heating. Again, the lack of path effects in the CAP or SOCAP model mean that for the same heating or cooling rate, the CAP or SOCAP will be the same for heating as cooling (over the same temperature range). Results for simulated heating or cooling between 350 and 973 K over 10 h are shown in Figure 12. For both heating and cooling, the evolution of mean radius (Figure 12(a–b)) has entered the coarsening dominated regime at the end of the simulation. It is striking that although the radius evolution follows a different pathway for heating or cooling, the final radius values are almost identical in both cases (55 nm). The solute concentrations in the matrix at the end of the simulations are slightly different (Figure 12 (c–d)) since on heating the equilibrium solubility increases whilst on cooling it reduces. Nevertheless, the difference is small compared to the initial (fully supersaturated) solute concentration. Again, therefore, the CAP or SOCAP approximations may be reasonable in this case, even though they ignore the difference in path between heating and cooling. Note that this is only valid because by the end of the heating or cooling cycle, coarsening has become well established.

One application of the CAP or SOCAP methods is to find an equivalent isothermal heat treatment that can mimic a complex thermal pathway, and thus allow simple isothermal test data (e.g. from autoclave testing) to be directly applied to the complex industrial case. To evaluate the validity this approach for an example case, the model was run for isothermal treatment at 673 K, and the radius and matrix solute level were compared against those previously predicted at the end of complex thermal paths discussed previously for the same value of the CAP. The results are shown in Figure 13. This exercise was also repeated using the SOCAP parameter, but the level of agreement was not improved and the results are omitted for brevity. Looking first at the mean radius evolution (Figure 13 (a)), it can be seen there is excellent agreement between the predicted radius for the isothermal exposure and that for the complex treatments at the same CAP value once coarsening has become well established ($\text{CAP} > 10^{-5}$). The CAP values for all of the non-isothermal treatments considered in this study (except for $\beta$-quenching) fall within this coarsening dominated range. Therefore, for these treatments, the application of cumulative annealing parameter (or SOCAP) to make comparisons with isothermal experiments will be reasonable, assuming that SPP size is the controlling microstructural variable.

In the case of matrix solute level (Figure 13(b)), the temperature at the end of the complex thermal path also becomes important since the same CAP
Figure 12: Predicted evolution of mean SPP radius (a–b) for (a) cooling at a constant rate from 350 and 973 K over 10 h, (b) heating over same range. Predicted evolution of solute in matrix (c) cooling at a constant rate from 350 and 973 K over 10 h, (d) heating over same range.
values can lead to different solute levels depending on the final temperature for a complex thermal path. However, providing the CAP is sufficiently large for coarsening to become established, and the temperature at the end of the multi-step process is reasonably close to the isothermal temperature (e.g. within 50 K), then the iso–CAP condition will give a good approximation to the matrix solute level.

4. Conclusions

This paper has used a physics based model for second phase particle (SPP) evolution to test the validity of the cumulative annealing parameter (CAP), particle growth parameter (PGP), and second order annealing parameter (SOCAP) approaches that are widely applied to interpret phenomena in Zircalloys that relate to SPPs (e.g. corrosion resistance). The following conclusions may be drawn from this work:

- Annealing parameter approaches implicitly or explicitly assume that SPP evolution is dominated by coarsening, with a temperature dependency that can be captured by a single activation energy. Compared with a physics based prediction of SPP evolution including nucleation and growth, it is demonstrated that the CAP, PGP, and SOCAP methods are valid in the coarsening regime, but not prior to this.
Prior to the onset of SPP coarsening, the mean SPP radius and particle size distribution can be very different at different temperatures, even for the same value of CAP, PGP, or SOCAP.

Annealing parameter approaches require that for any temperature, the microstructural parameter of interest will be constant for iso-annealing parameter conditions. This is demonstrated to be true for the mean particle radius once the coarsening regime is reached.

The complex thermal treatments typically applied in the industrial processing of zircalloys (e.g. relatively slow $\beta$-quenching, or multi-step annealing) are predicted to be sufficient in time and temperature to enter the coarsening dominated regime for SPP evolution. Therefore, annealing parameter approaches are justified for the industrial processing of Zircalloys.

Annealing parameter approaches ignore path effects when considering non-isothermal treatments. However, it is demonstrated that for the heating rates and temperatures that are typical of those in industrial processing of Zircalloys, the practical effect of this approximation is predicted to be small. This is because once the coarsening regime is well established, the mean SPP radius and particle size distribution tend towards path independent values.

Annealing parameter methods are demonstrated to be practically useful in application to Zircalloys but should not be applied without consideration of their limitations. In particular, it is important to establish that the SPP evolution is in the coarsening dominated regime before application of these methods. A physical SPP evolution model such as that presented here can be a useful tool to confirm this.

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6. Data availability

The data presented in this paper are available from Zenodo (zenodo.org).

[1] F. Garzarolli, H. Stehle, E. Steinberg, Behavior and properties of zircalloys in power reactors: A short review of pertinent aspects in LWR fuel, Zirconium in the Nuclear Industry: Eleventh International Symposium (1996) 12–32.

[2] G. Maussner, E. Steinberg, E. Tenckhoff, Nucleation and growth of intermetallic precipitates in Zircaloy-2 and Zircaloy-4 and correlation to nodular corrosion behavior, Zirconium in the Nuclear Industry: Eighth International Symposium (1987) 307–320.

[3] F. Garzarolli, E. Steinberg, H. G. Weidinger, Microstructure and corrosion studies for optimized PWR and BWR zircaloy cladding, Zirconium in the Nuclear Industry: Eighth International Symposium (1989) 202–212.

[4] T. Thorvaldsson, T. Andersson, A. Wilson, A. Wardle, Correlation between 400°C steam corrosion behavior, heat treatment, and microstructure of Zircaloy-4 tubing, Zirconium in the Nuclear Industry: Eighth International Symposium (1989) 128–140.

[5] E. Steinberg, H. Weidinger, A. Schaa, Analytical approaches and experimental verification to describe the influence of cold work and heat treatment on the mechanical properties of Zircaloy cladding tubes, Zirconium in the Nuclear Industry: Eighth International Symposium (1984) 106–122.

[6] D. Charquet, E. Steinberg, Y. Millet, Influence of variations in early fabrication steps on corrosion, mechanical properties, and structure of Zircaloy-4 products, Zirconium in the Nuclear Industry: Eighth International Symposium (1987) 431–446.

[7] M. Limbäck, T. Andersson, A model for analysis of the effect of final annealing on the in-and out-of-reactor creep behavior of zircaloy cladding, Zirconium in the Nuclear Industry: Eleventh International Symposium (1996) 448–468.
[8] J. H. Baek, Y. H. Jeong, I. S. Kim, Effects of the accumulated annealing parameter on the corrosion characteristics of a Zr–0.5 Nb–1.0 Sn–0.5 Fe–0.25 Cr alloy, Journal of Nuclear Materials 280 (2) (2000) 235–245.

[9] M. Gass, M. Fenwick, H. Hulme, M. Waters, P. Binks, A. Panteli, M. Chatterton, V. Allen, A. Cole-Baker, Corrosion of Zircalloys: Relating the microstructural observations to the corrosion kinetics, Journal of Nuclear Materials 509 (2018) 343–354.

[10] J. P. Gros, J. F. Wadier, Precipitate growth kinetics in Zircaloy-4, Journal of Nuclear Materials 172 (1) (1990) 85–96.

[11] M. Kahlweit, Further considerations on the theory of aging (ostwald ripening), Berichte der Bunsengesellschaft für Physikalische Chemie 78 (10) (1974) 997–1001.

[12] J. W. Christian, The Theory of Transformations in Metals and Alloys, Elsevier, 2002.

[13] J. Robson, Modeling precipitate evolution in zirconium alloys during irradiation, Journal of Nuclear Materials 476 (2016) 123–131.

[14] J. Robson, P. Prangnell, Modelling Al$_2$Zr dispersoid precipitation in multicomponent aluminium alloys, Materials Science and Engineering: A 352 (1-2) (2003) 240–250.

[15] R. Wagner, R. Kampmann, Homogeneous second phase precipitation, Phase Transformations in Materials 5 (1991) 213–303.

[16] A. Massih, L. Jernkvist, Nucleation and growth of second-phase precipitates under quenching and annealing, Computational Materials Science 39 (2) (2007) 349–358.

[17] J. D. Robson, Modelling the evolution of particle size distribution during nucleation, growth and coarsening, Materials Science and Technology 20 (4) (2004) 441–448.