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UCRL-CONF-200741

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Michael P. Surh, Taira Okita, Wilhelm G. Wolfer

November 4, 2003

11th International Conference on Fusion Reactor Materials
Kyoto, Japan
December 7, 2003 through December 12, 2003

#04A P.O.43

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Michael P. Surh, T. Okita and W. G. Wolfer

Lawrence Livermore National Laboratory

7000 East Ave. Livermore, CA, 94550, USA

Corresponding author: Michael P. Surh

TEL: +1-925-422-2087

FAX: +1-925-423-7040

E-mail: surh1@llnl.gov

Abstract

Standard rate theory methods have recently been combined with experimental microstructures to successfully reproduce measured swelling behavior in ternary steels around 400 C. Fit parameters have reasonable values except possibly for the recombination radius, R_c, which can be larger than expected. Numerical simulations of void nucleation and growth reveal the importance additional recombination processes at unstable clusters. Such extra recombination may reduce the range of possible values for R_c. A modified rate theory is presented here that includes the effect of these undetectably small defect clusters. The fit values for R_c are not appreciably altered, as the modification has little effect on the model behavior in the late steady state. It slightly improves the predictions for early transient times, when the sink strength of stable voids and dislocations is relatively small. Standard rate theory successfully explains steady swelling behavior in high purity stainless steel.

Keyword codes: N0100, R0200, S0500, S1400, T0100

Introduction

Structural materials for blankets in fusion reactors will likely be exposed to high-energy neutron fluxes over extended periods. Predictive models for the resulting void swelling, irradiation creep, and changes in mechanical properties may be needed to help design these components in the absence of long-term experimental data. In the past, simple rate-theory approaches have been employed for modeling irradiation-induced microstructural evolution to tens of dpa. The simplest such model includes only three point defect reactions, namely vacancy-interstitial recombination, monomer absorption at sinks, and thermal emission of vacancies from sinks. Despite its approximations, rate theory can successfully reproduce observed void swelling for the pure austenitic ternary alloys using realistic model parameters that are consistent with expectations from theory and experiment [1].

Swelling in Fe-15Cr-16Ni irradiated in FFTF at 408 – 444˚C has recently been measured at two successive, cumulative doses for a wide range of dose rates [3,4]. The swelling across the second cycle is ~ 1%//dpa, indicating that the experiments have exceeded the incubation dose [5]. These swelling measurements are augmented by detailed microstructural observations for each data point, including size distributions and densities of cavities, dislocation loops, and network dislocations (not shown). These complementary sets of observations have been used to fit or constrain rate theory models for irradiation swelling, as well.

Based on the range of parameters obtained, rate theory suggests that the vacancy-interstitial recombination process may be more efficient than would be expected from microscopic arguments [2]. This seeming discrepancy might be reconciled in light of numerical simulations of void nucleation and growth. These studies reveal the influence of vacancy clusters that are undetectable to TEM, in addition to the usual, visible cavities and dislocations. The modified theory requires the density and aggregate sink strength for these small clusters that must currently be obtained from detailed numerical simulations, since the clusters are not visible to TEM. The unstable clusters slightly reduce the predicted swelling rates. However, they have little effect on the simple rate theory model in the steady state regime. Their effects are most noticeable at low doses. Thus, standard rate theory should give reliable estimates of material parameters in the steady state, whether or not unstable defect clusters are included.

For low temperatures, thermal emission may be neglected in the rate theory, which is assumed here for 400-440 C in austenitic stainless steel. The rate theory equations become:

$$\frac{dC_i}{dt} = P_i - \alpha D_v C_v D_i C_i - \left(\sum_u N^u A^u Z_i^{\,u}\right) D_i C_i - \left(\sum_s N^s A^s Z_i^{\,s}\right) D_i C_i - \left(\sum_d N^d A^d Z_i^{\,d}\right) D_i C_i$$

$$\frac{dC_v}{dt} = P_v - \alpha D_v C_v D_i C_i - \left(\sum_u N^u A^u Z_i^{\,u}\right) D_i C_i$$
$$- D_v\left(\sum_s N^s A^s Z_v^{\,s}(C_v - C_v^{eq(s)})\right) - D_v\left(\sum_d N^d A^d Z_v^{\,d}(C_v - C_v^{eq(d)})\right)$$

where subscripts *v* and *i* denote mobile vacancies and interstitials; *D* are diffusivities; and the vacancy interstitial annihilation rate constant is

$$\square = 4\pi R_c\left(\frac{1}{D_v}+\frac{1}{D_i}\right).$$

Defect clusters are separated into stable (large) and unstable (small) voids and dislocations with size-dependent bias factors denoted *Z*. The cross-section for monomer-cluster aggregation in the absence of long-range interactions is *A*. Dislocation parameters in the rate equations are denoted by superscripts *d*. The cavity contribution is separated into stable and unstable populations, u and s, respectively. The experimentally measured cluster population gives N_h , the cavity density versus size, *h*, or radius, a_h for visible clusters only.

Unstable clusters are included in the vacancy equation in an unconventional manner. It is important to recognize that the distribution of unstable clusters is quasi-stationary. That is, cluster size fluctuates very rapidly for the small clusters. For all but the earliest part of the irradiation transient, the sub-critical population reaches a limit in which its aggregate volume neither grows nor shrinks appreciably (compared to the rate of growth of the stable voids). These unstable clusters continue to absorb defect monomers, but in almost exactly equal numbers of vacancies and interstitials, on average. Thus, the net vacancy flux can be replaced with the expression for the interstitial flux. In effect, the unstable clusters catalyze an indirect recombination of vacancies and interstitials, in an average sense.

A representative calculation for interstitial-biased sink strengths of stable, visible voids and unstable, undetectable clusters is shown in Fig. 1. The simulation corresponds to high purity stainless steel at 420 C, with a dislocation content of 6×10^{14} m^{-2}. The elapsed time is not important; rather, what matters is that the unstable sink strength is controlled by the instantaneous strength of the dislocations and stable voids. These unstable clusters are sustained by the non-equilibrium population of defect monomers, and are present in both the incubation and steady-state swelling regimes, depending on the sink strength of other elements of the microstructure. For the experimental microstructures, the unstable cluster sink strength will lie between 6×10^{14} m^{-2} and 9×10^{14} m^{-2}. The unstable cluster value is set to 8×10^{14} m^{-2}, for all of the modified rate theory calculations. This is reasonable for late times, but it may underestimate their effect early in the irradiation, when the stable clusters have a relatively small sink strength.

When the microstructure data obtained by the FFTF experiments are used in the rate equations, some parameters remain undetermined. These include the cascade efficiency η and defect production rate, P (equal to η times the dose rate in dpa); the vacancy migration energy E_v (controlling the diffusivity); the interstitial bias factors for faulted loops Z^{fl} and network dislocation Z^{d}; and the recombination radius for point defects R_c. These parameters must fall within a range of acceptable values, based on microscopic arguments (1.2 eV $\leq E_v \leq$ 1.4 eV [6,7], 1.1 $\leq Z \leq$ 2.0 [8-10], 2.0 $a_0 \leq Rc \leq$ 7.0a_0 [2], and 0.1 $\leq \eta \leq$ 0.2 [11]). The bias factors for voids are approximated as equal to 1.0, as are the dislocation-vacancy bias factors.

At least in pure ternary austenitic alloys, the standard rate theory can explain the swelling rate quite well. Table 1 summarizes the results of the model based on a single, typical fit. Generally, variation in one parameter requires changes in others. The fit procedure thus obtains multiple sets of theoretically plausible material parameters. In some cases, the vacancy-interstitial recombination radius is larger than expected. Values as large as 7.0 a_0 are possible, much larger than the estimation of 2.0 a_0 obtained from theoretical arguments. This suggests that the vacancy-interstitial recombination process is more efficient than calculations for vacancy-interstitial interactions would allow.

This tendency is consistent with recent numerical simulations of cavity nucleation and growth, which include a population of sub-critical vacancy clusters. These invisible recombination sites can enhance the overall rate of vacancy-interstitial annihilation. A rate theory has been constructed for this model, which also agrees well with experiment. In practice, the rate theory is very insensitive to these changes, except possibly at the very earliest times during the irradiation transient.

Results of the modified rate theory model

In the quasi-stationary limit, the time-derivatives of the monomer concentrations are essentially zero. The solution to their coupled, quadratic rate equations is then easily obtained [1]. Defining $\overline{\square^d} = \sum_d Z^d A^d N^d$, $\overline{\square^s} = \sum_s Z^s A^s N^s$,

$\overline{\square} = \underset{x=s,d}{\square} Z^x A^x N^x$, and $\overline{Z_v}\overline{C_v^{eq}} = \underset{x=s,d}{\square} Z^x A^x N^x C_v^{eq(x)}$ gives a quadratic equation with solution:

$$
\begin{aligned}
D_i C_i &= \frac{1}{2}\left(\sqrt{M^2 + L} \,\square\, M\right) \\
M &= D_v \overline{C_v^{eq}} \frac{\overline{\square_v}}{\overline{\square_i}} + \frac{(P_v \,\square\, P_i)}{\overline{\square_i}} + \frac{\overline{\square_v}}{K} \frac{(\overline{\square_i^u} + \overline{\square_i})}{\overline{\square_i}} \\
L &= \frac{4P_i}{K} \frac{\overline{\square_v}}{\overline{\square_i}}
\end{aligned}
$$

The vacancy concentration is obtained from:

$$
D_v C_v = \frac{P_v \,\square\, P_i}{\overline{\square_v}} + D_i C_i \frac{\overline{\square_i}}{\overline{\square_v}} + D_v \overline{C_v^{eq}}
$$

There is no production bias considered here, so that P_v=P_i. The solution can be reduced to the standard rate theory by simply setting the unstable cluster sink strength to zero. They merely make an additive contribution to the total sink strength in the quantity *M*.

Finally, the swelling rate is obtained from the net flux of interstitials (minus vacancies) to the dislocations. All vacancy emission is neglected for low temperatures, so that:

$$
\frac{d}{dt}\frac{\square V}{V} = D_i C_i \overline{\square_i^d} \,\square\, D_v C_v \overline{\square_v^d}
$$

in terms of average quantities for the dislocation population.

Measured swelling rates are shown in Table 1, along with the results of a single fit parameter set. The measured swelling rate "□swelling" is based on the volume difference between the two successive observations. Model predictions are obtained at both the lower and upper dose points (both “standard” and “modified” rate theories). The standard rate theory can agree quite well with the experimental results. The modified rate theory similarly agrees with the available swelling data. It gives a slightly lower swelling rate, which could be compensated by adjusting the model parameters. The unstable clusters do influence transient behavior, when the unstable cluster sinks can dominate the stable voids and dislocations. (It can be seen that the relative reduction in swelling rate is larger at the top of the table, which corresponds to samples with lower doses.) Here, the modified rate theory displays more realistic swelling behavior. Because the swelling curves are concave upwards, the predicted instantaneous swelling should be lower at the first point than the finite difference result. Similarly, the instantaneous rate should be higher at the second observation point. This behavior is better achieved with the modified rate theory.

Summary

The standard, simplified rate theory for swelling in Fe-15Cr-16Ni may suggest a larger recombination radius then is expected from reaction-diffusion calculations. When the rate theory is extended so that recombination can occur at invisible defect sites, the modification is found to have little effect on the fit. This suggests that the rate theory is useful in its standard form at moderate temperatures and higher and especially in the steady state, where the concentration of small, unstable clusters is low. The modified rate theory may be needed more during the incubation period, when undetectable clusters are more prevalent.

Acknowledgments

The authors gratefully acknowledge support of this work by a NERI grant from the U.S. Department of Energy under contract W-7405-ENG-48 with the Lawrence Livermore National Laboratory.

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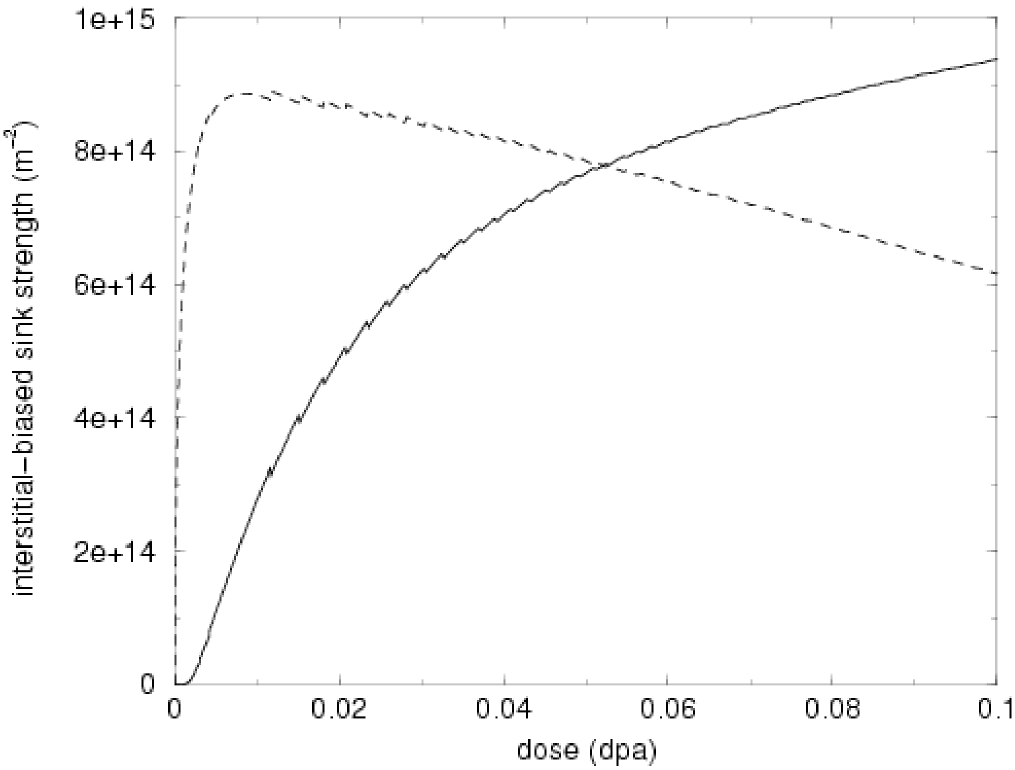
Table 1. Experimental swelling versus the model results for one possible parameter set. The rates labeled "Δswelling" are obtained by finite differences of the two successive swelling measurements in paired samples. The "standard" and "modified" results refer to the respective rate theory predictions for a single, reasonable parameter set (set #1 in Ref. [1]).

dose rate	Cumulative dose	swelling	Δswelling (%/dpa)	standard (%/dpa)	modified (%/dpa)
8.9×10^{-9}	0.23	0.0106	0.24	0.49	0.10
2.2×10^{-8}	0.61	0.101		0.78	0.27
2.7×10^{-8}	0.71	0.0761	0.74	0.75	0.27
6.6×10^{-8}	1.87	0.934		1.10	0.64
9.1×10^{-8}	2.36	0.515	0.81	1.00	0.55
2.1×10^{-7}	6.36	3.77		1.11	0.80
3.1×10^{-7}	8.05	2.21	0.96	1.09	0.77
3.0×10^{-7}	11.1	5.14		1.16	0.89
5.4×10^{-7}	14.0	3.97	1.06	0.94	0.70
8.4×10^{-7}	28.8	19.7		0.82	0.66
7.8×10^{-7}	20.0	5.36	0.93	0.79	0.62
9.5×10^{-7}	32.4	16.9		0.87	0.71

Figure Captions

Figure 1 Simulated sink strengths for stable voids (solid line) and unstable clusters versus dose for a type-316 stainless steel at 420 C. The jaggedness of the lines results from discrete changes in the critical cluster size as the monomer concentration evolves with time. Unstable cluster sinks dominate the system until the dislocation and stable voids rise to appreciable values.



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