



The mechanism of radiation-induced segregation in ferritic–martensitic alloys

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Abstract

The mechanism of radiation-induced segregation in Fe–Cr alloys was modeled using the inverse Kirkendall mechanism and compared to experimental measurements over a range of temperatures, bulk Cr compositions, and irradiation dose. The model showed that over a large temperature range chromium was enriched at sinks by interstitial migration, and at very high temperatures it was depleted by diffusing opposite to the vacancy flux. Experimental results and model predictions were in good qualitative and quantitative agreement with regard to the temperature dependence of segregation and the crossover from Cr enrichment to Cr depletion. The inverse Kirkendall mechanism was also in agreement with experimental findings that observed a decreasing amount of Cr enrichment with increasing bulk Cr composition. The effects of solute drag were modeled within the inverse Kirkendall framework, but were unable to account for either the crossover from Cr enrichment to Cr depletion or the magnitudes of segregation measured in experiments.

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1. Introduction

The renewed interest in nuclear energy as a source of carbon-free electricity has reinvigorated research on the effects of irradiation in ferritic–martensitic (F–M) alloys, which are the leading candidates for cladding and structural components in some advanced nuclear reactor concepts. These steels have high strength at elevated temperatures, are resistant to thermal stresses and are dimensionally stable under irradiation [1]. However our understanding of nucleation and growth of defect clusters (loops, voids), phase stability, radiation-induced segregation and irradiation creep is lacking. Radiation-induced segregation (RIS), in particular, suffers from very few and conflicting observations, confounding a mechanistic understanding of its origin.

Lu et al. [2] recently surveyed the literature on the RIS behavior of F–M alloys and identified only 15 experimental studies on RIS in a variety of model and commercial F–M alloys (5–13% Cr), irradiated over a range of temperatures (250–800 °C), doses (0.5–118 dpa), and fluxes (10^{-5} – 10^{-1} dpa s⁻¹), and with a variety of irradiating particles. Lu et al.'s survey revealed small amounts of Cr enrichment (<5 wt.% Cr) at grain boundaries in some studies and depletion in others. Given the inconclusive, inconsistent data and the varying conditions under which the experiments were performed, it was impossible to extract trends in the data or any mechanistic understanding of RIS. The finding of grain boundary Cr enrichment in F–M alloys was contrary to the highly consistent and repeatable measurements of Cr depletion in austenitic alloys, which has been accurately predicted by the inverse Kirkendall (IK) mechanism [3]. Thus, the IK mechanism was initially suspected to be irrelevant to F–M alloys. Until this work, however, a thorough investigation of the IK mechanism using material parameters appropriate for

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body-centered-cubic (bcc) Fe–Cr alloys, had not been performed. Other mechanisms were investigated in attempts to explain the inconsistent experimental results of Cr RIS.

The solute drag mechanism, in which tightly bound solute-defect complexes diffuse significant distances before dissociating, was proposed as a possible mechanism of RIS in F–M alloys. However, most investigations of the solute drag mechanism [4–7] focused on minor elements such a P, S and B rather than on major alloying components like Cr in Fe.

Recent modeling efforts calculated attractive binding energies between Cr atoms and vacancies as well as between Cr atoms and interstitials [8–10], suggesting that Cr would enrich via solute drag. Prior to this work, only Johnson and Lam [11,12] had accounted for the effects of solute drag in a rate theory (i.e. IK-type) model, but their results were inconclusive and were presented only for ternary face-centered cubic (fcc) Fe–Cr–Ni systems.

Recent work has suggested a link between RIS in Fe–Cr alloys and atomic-level electronic and magnetic properties, manifest as a change of sign of mixing enthalpy near 10% Cr [13–18]. These models reinforced experimental observations [19–21] that at low Cr concentrations, Cr atoms order as far apart from one another as possible [15,22], but with increasing Cr concentration, Cr–Cr interactions become unavoidable, leading to positive formation enthalpy [22]. This theory offers a plausible explanation for why high-Cr steels would have clusters, precipitates and grain boundaries enriched in Cr. However, mixing enthalpy cannot explain the underlying mechanism of RIS, since it does not consider how atomic species are transported toward or away from grain boundaries, nor can it explain Cr enrichment in low-Cr steels, as observed in Refs. [23,24].

The solute size effect has also been addressed. Wong et al. [8] and Choudhury et al. [10] calculated that Cr is an undersized solute in the Fe matrix, while Terentyev et al. [25] calculated that Cr is oversized. Lu et al. [2] also argued the solute size effect, based upon atomic radii differences, suggesting that with increasing concentrations of oversized impurities (e.g. W, Nb, Mo, Ti), the relative size of Cr, and thus the tendency of Cr to deplete, decreases.

While a number of theories for Cr RIS in bcc Fe–Cr alloys have been proposed and investigated, none could consistently and comprehensively explain experimental observations. In addition, it was not until Wharry and Was [24] presented the first systematic experimental study of RIS in F–M alloys, that the dependencies of RIS on irradiation parameters and on Cr content could be established. The authors found small amounts of Cr enrichment (<2 wt.%) in all but one dose/temperature condition, and found that Cr enrichment followed a bell-shaped temperature dependence. In T91 irradiated to 3 dpa, Cr enrichment was at a minimum at 300 °C and 600 °C, and a maximum at 450 °C; Cr depletion only occurred at 700 °C. The extent of Cr enrichment decreased with increasing bulk Cr content, following 400 °C irradiation to 3 dpa. Lastly, the authors found little dose dependence of Cr RIS in T91 irra-

diated at 400 °C to 1, 3, 7 and 10 dpa. Understanding these systematic variations of RIS with key parameters is a prerequisite to identifying the mechanism(s) driving RIS and in developing a predictive model.

This paper aims to determine the mechanism of RIS in a binary Fe–Cr (bcc) system by comparing model calculations of RIS based on the IK mechanism against experimental measurements. Since the IK mechanism is both well known and has been applied to austenitic Fe–Cr–Ni alloys, it is selected as the reference case for investigation of RIS in bcc Fe–Cr alloys. The effects of solute drag will then be incorporated into the IK model. Model calculations will be compared to the experimental measurements presented in Ref. [24]. Model–experiment comparisons will demonstrate whether RIS in F–M alloys is consistent with the IK and solute drag mechanisms. Finally, experimental measurements of RIS published in the open literature will be considered in the context of the results of this paper.

2. Inverse Kirkendall model for binary Fe–Cr alloys

The purpose of this section is to describe the inverse Kirkendall modeling methodology for Fe–Cr alloys and the sensitivity of variables to input parameters. Appropriate input parameters will be chosen for an Fe–9Cr bcc alloy system. Finally, the method for comparing model results to experimental measurements will be described.

2.1. The inverse Kirkendall model

The one-dimensional (1-D) inverse Kirkendall model used in this study was based upon the framework of the Perks [26,27] rate theory model. In this framework, a system of equations representing the concentrations of the major alloying elements and the point defects is solved simultaneously as a function of space and time. These equations are written for a binary A–B alloy as:

$$\frac{\partial C_A}{\partial t} = \nabla [D_A \alpha \nabla C_A + N_A (d_{Av} \nabla C_v - d_{Ai} \nabla C_i)] \quad (1)$$

$$\frac{\partial C_B}{\partial t} = \nabla [D_B \alpha \nabla C_B + N_B (d_{Bv} \nabla C_v - d_{Bi} \nabla C_i)] \quad (2)$$

$$\frac{\partial C_i}{\partial t} = \nabla [-d_{Ai} N_i \alpha \nabla C_A - d_{Bi} N_i \alpha \nabla C_B + D_i \nabla C_i] + K_0 - R - S_i \quad (3)$$

$$\frac{\partial C_v}{\partial t} = \nabla [d_{Av} N_v \alpha \nabla C_A - d_{Bv} N_v \alpha \nabla C_B + D_v \nabla C_v] + K_0 - R - S_v \quad (4)$$

Eqs. (1)–(4) represent the time rate of change of the concentrations of atoms A and B, interstitials and vacancies, respectively, at a fixed position in space. The right-hand sides of Eqs. (1) and (2) represent the positional flux of the given atomic specie. The right-hand sides of Eqs. (3) and (4) consider defect production (K_0), loss of defects to recombination (R) and sinks (S_i or S_v), and the positional flux of defects (bracketed terms). In all of the above equations, variables are concentration C , time t , diffusion coefficients D , diffusivities d , number density N and

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