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Thermodynamic and kinetic modeling of oxide precipitation in nanostructured ferritic alloys

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Abstract—The mechanical properties and radiation tolerance of nanostructured ferritic alloys rely on a dense population of nanometer-scale Y–Ti oxides. The stability of these nano-oxides during extended service is critical in high temperature applications. Here, a model framework is developed for the thermodynamics and kinetics of Y–Ti oxide nucleation, growth and coarsening. The model, which is based upon available thermodynamic and kinetic data as well as key density functional theory calculations, shows that nano-oxide nucleation and growth are highly driven and that pipe diffusion is the dominant mode of their coarsening, in agreement with previous analyses of experimental high temperature data. The model predicts that the nano-oxides are thermally stable for 80 or more years below 1175 K. This analysis also provides insights into the effect of O and Ti on nano-oxide sizes, and on optimization of alloy microstructure.

Keywords: Nucleation; Growth; Phase equilibria; Theory and modeling; Steels

1. Introduction

Future advanced nuclear energy systems are expected to place demands on structural materials that lie well beyond the capabilities of materials used in current reactors. Structural materials in proposed fusion and many advanced fission reactor designs would be subject to significantly higher operating temperatures and much larger radiation doses than their counterparts in conventional light water reactors. Nanostructured ferritic alloys (NFAs), which are a variant of oxide dispersion strengthened (ODS) steels, are a uniquely promising candidate alloy class to meet these demanding requirements [1–5].

NFAs typically contain (in wt.%) 12–16 Cr and up to 0.5 Mo or 3 W [10] with small additions Ti, Y, and O. The latter solutes precipitate during processing to form a high density of Ti–Y–O nano-oxides. The Y and some O are most often introduced by mechanically alloying Y_2O_3 with ferritic steel powders using high energy ball milling. The alloy powders are then consolidated by hot isostatic pressing or extrusion.

The Y–Ti oxides are highly effective in pinning dislocations and constitute a high density of point defect sinks that also trap transmutant helium. These functions lead to both outstanding high temperature strength and irradiation tolerance [2]. Thus, the ability to produce optimal nano-oxide distributions during processing, and their subsequent stability and resistance to excessive coarsening during service, are critically important issues [6,7,10]. Predicting nano-oxide coarsening over decades of service is particularly challenging since such predictions must be based on relatively short-time experiments. Therefore, a primary motivation for the present study is to develop physically-based models that can provide qualitative and quantitative insight into the nano-oxide thermodynamics and kinetics that mediate phase selection, precipitation and coarsening. Due to the complexity of the many interactive processes being treated, a small number of fit parameters are required to fully calibrate the models. The fit parameters include the effective values of the chemical potential of oxygen in solution and the oxide-ferrite interface energies. The fitting strategy is described in detail below. Other parameters have been estimated based on direct experimental measurements or generally observed empirical trends. While this approach leads to some uncertainties in the model predictions, they do not have a significant impact on the major conclusions and mechanistic insights reached in this study related to the active mechanisms during nano-oxide evolutions and how Y–Ti–O composition and thermal history determine precipitate phases, sizes and number densities.

Due to their very small size, there is some uncertainty regarding nano-oxide structures and compositions. Most

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high-resolution TEM studies show that the nano-oxides are consistent with $Y_2Ti_2O_7$ [8–10]. Combined small angle neutron and X-ray scattering [10–12] and X-ray diffraction measurements [13,14] are also broadly consistent with this conclusion. However, the $Y_2Ti_2O_7$ may not be fully stoichiometric; and a multitude of other observed oxide phases include, but are not limited to, Y_2TiO_5, Y_2O_3, $CrTiO_3$ and TiO_2, as well as a variety of carbo-nitrides. Atom probe tomography (APT) measurements have been interpreted to indicate that the smallest Y–Ti–O are coherent highly non-stoichiometric sub-oxides with high Ti/Y ratios [1,11,15–21]. However, it is likely that the APT atom probe measurements are affected by various artifacts [10]. Furthermore, density functional theory (DFT) calculations of the formation energies of small Y–Ti–O clusters in Fe have shown that small clusters that are structurally similar to bulk Y and T–Ti oxides are far more stable than clusters that are coherent with the ferrite matrix [22]. Here, we assume that the nano-oxides are known equilibrium Y–Ti–O phases during their entire evolution.

A second major complication in developing a model is associated with the fact that O contents in NFAs are far in excess of equilibrium values. Indeed, non-equilibrium O concentrations in excess of that added by Y_2O_3 are needed to produce optimal Y–Ti nano-oxides [23]. As the concentration of O within the alloy is difficult to control, and likely fluctuates over the course of alloy processing, we use the O chemical potential within the alloy as an adjustable parameter in the model. Values representing equilibrium with possible Cr, Fe, and Ti oxides provide a plausible range of values for this parameter, along with precipitation and aging kinetics that are consistent with experimental observations. While these assumptions and approximations do not capture all of the potentially important physics, such as the precise nucleation pathway through compositional space, or the appearance of metastable phases, they provide a well-defined foundation to begin to understand the complex multicomponent precipitation process in nanostructured ferritic alloys.

The remainder of this paper is organized as follows: Section 2 details the thermodynamic model used to evaluate the necessary driving forces for modeling nano-oxide precipitation and coarsening. The kinetic model for simulating nano-oxide precipitation is then briefly described, with additional details found in the Appendix A. Section 3 presents the predictions of the thermodynamic model and the results of fitting the kinetic model to experimental measurements of nanoparticle size as a function of aging time. The predictions of the best-fit model for both coarsening kinetics and alloy composition effects on nanoparticle size are then described. Finally, Section 4 provides concluding remarks and commentary on paths that can lead to more advanced models.

2. Methods

2.1. Thermodynamic model

The model developed in this study describes phase separation of Y and Ti nano-oxide phases from a bcc Fe–Cr–Y–Ti solid solution. The thermodynamic model used to describe this process includes the following phases: bixbyite Y_2O_3, rutile TiO_2, pyrochlore $Y_2Ti_2O_7$, orthorhombic Y_2TiO_5, and ferrite Fe–Cr–Y–Ti solid solution. These oxides are the equilibrium phases in the $Y_2O_3 - TiO_2$ pseudobinary system [24] over the temperature range of interest (900–1573 K), while ferrite is the matrix phase in the NFAs considered in this study with Cr contents lying outside the gamma loop [2,25].

The thermodynamic equilibrium phase separated state of a given NFA can be determined by first computing the free energies of the individual phases listed above and then minimizing the total free energy of the system as mediated by the fractions of each phase. Numerous thermodynamic assessments in the CALPHAD formalism were used to describe these free energies. The necessary parameters for these descriptions are summarized in Table 1.

The total free energy to be minimized may be written as

$$G^{\mathrm{tot}} = f^{\alpha}G^{\alpha} + f^{203}G^{203} + f^{227}G^{227} + f^{215}G^{215} + f^{012}G^{012} \tag{1}$$

where f^iG^i is the product of the mole fraction of phase i and the molar free energy of phase i. The superscripts 203, 227, 215, and 012 refer to the oxide phases Y_2O_3, $Y_2Ti_2O_7$, Y_2TiO_5, and TiO_2, respectively. The free energy of the solid solution phase is computed using the following equation

$$G^{\alpha} = \sum_i x_i {}^{0}G_i^{\alpha} + RT\sum_i x_i \ln x_i + {}^{\mathrm{ex}}G^{\alpha} \tag{2}$$

where x_i is the mole fraction of component i in the ferrite phase α (i = Y or Ti), and ${}^{0}G_i^{\alpha}$ is the molar free energy of pure component i in the structure of α. The term ${}^{\mathrm{ex}}G^{\alpha}$ is the excess free energy of mixing, described by the Redlich–Kister polynomial

$${}^{\mathrm{ex}}G^{\alpha} = x_m x_n \sum_j (x_m - x_n)^{j\,(j)}L_{mn}^{\alpha} \tag{3}$$

where m = Fe, Cr and n = Y, Ti. The parameters ${}^{(j)}L_{mn}^{\alpha}$ are the Redlich–Kister polynomial expansion coefficients and are evaluated in Table 1. Because the mole fractions of Ti and Y in NFAs are generally dilute (typically less than 1 at.%), Y–Y, Y–Ti, and Ti–Ti interactions in the solid solution phase are neglected. Furthermore, because their mole fractions in solution do not change significantly during the precipitation of the Y and Ti oxide phases, the Fe and Cr contributions to total free energy are approximately the same before and after the phase separation, and thus are neglected. Finally, it is assumed that O exists in the alloy at a constant chemical potential throughout phase separation. This chemical potential value determines the driving force for oxide precipitation, and the detailed interactions of O within the solid solution phase are not required. This assumption is discussed further below.

The equilibrium oxide phase separation in a given NFA is found by minimizing Eq. (1) under the constraints of constant mole fractions of Fe, Cr, Y, and Ti, and a constant chemical potential of O. These constraints are equivalent to assuming that the system is closed with respect to the metallic constituents, but open with respect to O. The assumption of openness is based on ubiquitous observations that the initially dissolved O in NFA significantly exceeds the nominal solubility in equilibrium with the oxides of Fe, Ti and Cr [4–9]. The precise value of this O chemical potential is unknown. However, there are two important empirical constraints on the magnitude of the O chemical potential: (a) consistency with observed oxide phases in NFAs, which have well established *minimum* O