



# A thermodynamic and kinetic-based grain growth model for nanocrystalline materials: Parameter sensitivity analysis and model extension



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## ABSTRACT

Predicting grain growth in nanocrystalline materials requires modeling approaches that incorporate grain boundary thermodynamics and kinetics. In this work, the thermokinetic model of Chen et al. (2012) for grain growth was applied to experimental X-ray diffraction measurements from a binary nanocrystalline alloy in an effort (1) to understand the influence of thermodynamic, kinetic, and material parameters in the model; and (2) to extend the thermokinetic model by incorporating temperature dependence. The model performs well for the grain boundary saturated case in the binary nanocrystalline alloy, where it is assumed that solute segregates to the grain boundaries and thermodynamically/kinetically reduces the driving force for grain growth. In this work, a sensitivity analysis of parameters (Monte Carlo global sensitivity analysis) identifies the important thermodynamic/kinetic parameters and their correlation with one another for the present model. This model was then extended to include the change in these independent thermodynamic/kinetic parameters as a function of temperature and to model the effect of initial grain size distribution. This research shows that the thermodynamic and kinetic contributions can describe grain growth in nanocrystalline materials and this extended model can be parameterized for grain size evolution and stabilization with temperature for nanocrystalline systems.

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## 1. Introduction

The evolution of material microstructure during processing plays a commanding role in the physical properties and mechanisms in materials. Hence, establishing the processing-structure and structure-property relationships can help accelerate the design and development of new metals. Many materials already have a significant foundational understanding from decades of research, but emerging material classes such as nanocrystalline alloys are still not as well understood. Experimental studies are time-consuming and are therefore necessarily limited to a select number of compositions. Computational modeling has the potential to be quickly applied to many alloy systems, but the results should always be verified by experimental data. It is by marrying these two approaches that they can inform, and accelerate, one another. That is, computational results can be tuned by experimentally-derived parameters and experimental decisions can be informed by predicted results.

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Nanocrystalline alloys present an important subset of metallic materials [1]. Because of their small grain size (less than 100 nm), they tend to possess extremely high strengths [2–8], which are associated with grain boundary (GB) strengthening, i.e., the Hall–Petch effect [9,10]. Hence, these alloys can possibly enable new lightweight components, high-strength conductors, and many other applications that are not achievable using conventional coarse-grained alloys. A fundamental limitation to their use comes from their inherent thermal instability, which has been extensively explored using both experiments [11–19] and computational approaches [20–35]. The small grain size produces an extremely large driving force for grain growth. If not kept in check, grain growth can occur at modest temperatures, even at room temperature in pure materials, such as in copper and palladium [36]. Because nanocrystalline alloys are often produced via mechanical alloying [37,38], this grain growth phenomenon provides a significant obstacle to consolidating the nanocrystalline powders by traditional powder metallurgy techniques where high-temperature sintering is common.

There are several methods that have been devised to circumvent this temperature sensitivity and to stabilize the grain size.

Grain size stabilization commonly involves adding small quantities of an insoluble element (i.e., solute). Nonequilibrium processing (e.g., mechanical alloying, rapid solidification) is often used to force the solute into solution and, upon heating, the solute segregates to interfaces, such as GBs [39,40]. Alternatively, the solute remains in solution or precipitates out as a second phase. These 2 basic mechanisms for stabilization are known as thermodynamic stabilization and kinetic stabilization, respectively [41,20]. Thermodynamically, the solute is expected to segregate to GBs and reduce the GB energy, eliminating the driving force for growth [42]. Kinetically, the solute acts to hinder GB mobility by diffusion-related means, such as solute drag [43], or by pinning boundaries with a fine dispersion of precipitates [44].

The operating mechanism of stabilization can be difficult to delineate. Highly insoluble elements can segregate into interfaces, demix into discrete particles, or form intermetallic compounds with the solvent. The outcome depends on many different factors, such as elastic size mismatch between the solvent and solute and their enthalpy of mixing. To achieve thermodynamic stabilization, solute precipitation must be kinetically hindered [42]. Predicting and accounting for routes to grain size stabilization, then, is critical to deepening the understanding of grain size evolution in nanocrystalline alloys.

This work focuses on binary nanocrystalline alloys, using the iron–zirconium (Fe–Zr) system as an example. In this nanocrystalline system, experimental studies [14,16] have found that a nanoscale grain size can be maintained at 900 °C by adding 4 atomic percent (at.%, or just %) of the solute (Zr). Without the Zr addition, the grain size in nanocrystalline Fe starts to coarsen near 400 °C. Zr was chosen as a solute because of its large atomic size difference with Fe (28%) and its negative heat of mixing ( $-25 \text{ kJ mol}^{-1}$ ), which makes it more favorable for Fe and Zr to form bonds between one another than to form bonds between like atoms. Hence, intermetallic formation is a likely outcome at moderate-to-high temperatures. Intermetallic formation is also a likely outcome in regions with high concentrations of Zr (e.g., interfaces). The competition between atomic segregation and second phase formation suggests that binary nanocrystalline systems such as this must be considered from both thermodynamic and kinetic perspectives. In this manner, this nanocrystalline system is similar to many binary nanocrystalline systems. As such, it is considered to be a representative of the different potential microstructures within nanocrystalline systems and is used for the present study.

The objective of the present work is to formulate a predictive thermokinetic model for grain growth. This objective is accomplished by understanding parameter sensitivities of and extending the combined, thermokinetic model for grain growth [24,45,46] to allow for temperature dependence of these parameters, thereby extending this model's predictive capability over a wide range of temperatures. The extended model is used to predict grain growth at a variety of temperatures and solute concentrations in the Fe–Zr binary nanocrystalline system. The predictive modeling is then compared to X-ray diffraction data collected in situ during annealing of nanocrystalline Fe–Zr alloys with Zr (atomic) concentrations of 1% and 4%. The present work shows the benefit of adding temperature dependence to the thermokinetic model to predict grain growth for this system.

## 2. Simulation methodology: thermokinetic model

Grain growth of nanocrystalline materials can be characterized by the thermodynamic and kinetic contributions to stabilization [20]. First, the parabolic kinetics of grain growth are related to the presence of solute segregation to GBs and the drag force that

results. In this scenario, the GB velocity,  $V(= dD/dt)$ , is controlled by the motion of single atoms through

$$V = \frac{dD}{dt} = v\lambda_{\text{GBS}} \exp\left(-\frac{Q_d}{RT}\right) \left(1 - \exp\left(-\frac{\Delta P}{RT}\right)\right), \quad (1)$$

where  $v$  is the jump frequency,  $\lambda_{\text{GBS}}$  is the spacing of atoms in the GB,  $R$  is the gas constant,  $T$  is the temperature, and  $Q_d$  is the activation energy for an atom to transfer from 1 grain to another under a driving force  $\Delta P$ . We can assume that  $\Delta P \ll RT$  for most cases and that  $\Delta P \approx \gamma_b/D$  for curvature-induced grain growth processes, where  $\gamma_b$  is related to the GB energy. Additionally, the pre-exponential factor  $v\lambda_{\text{GBS}}/RT$  is related to the interface mobility  $M_0$ , leading to the expression

$$\frac{dD}{dt} = M_0 \frac{\gamma_b}{D} \exp\left(-\frac{Q_d}{RT}\right). \quad (2)$$

To calculate  $M_0$ , Vooijs et al. [47] showed that  $M_0 = v\lambda_{\text{GBS}}/RT = k\delta/hR$  with  $\delta = 3.0 \text{ \AA}$ , and  $h$  and  $k$  being the Planck's and Boltzmann's constants, respectively. This gives a mobility of  $0.7518 \text{ mol m J}^{-1} \text{ s}^{-1}$  that is only dependent on the length scale parameter relating to interface width,  $\delta$ . While these equations were originally used by Vooijs et al. [47] to describe the mobility of a phase boundary during the austenite to ferrite phase transformation, a similar mechanism exists for the mobility of grain boundaries, namely that boundaries move through a series of atom jumps in response to a driving force. Recent experiments and simulations have studied the velocities of these phase boundaries to better understand the relationships between phase boundary and grain boundary mobilities [48]. Despite some differences,  $M_0$  values in the range of  $0.75\text{--}0.80 \text{ mol m J}^{-1} \text{ s}^{-1}$  have been used with the thermokinetic model to describe stability in various nanocrystalline systems. In Eq. (2), both  $Q_d$  and  $\gamma_b$  are functions of the temperature  $T$  and the solute concentration  $x_0$ , giving

$$\frac{dD}{dt} = M_0 \frac{\gamma_b(T, x_0)}{D} \exp\left(-\frac{Q_d(T, x_0)}{RT}\right). \quad (3)$$

It can be shown that  $Q_d$  and  $\gamma_b$  are interrelated. For instance, as solute segregates to the boundary,  $\gamma_b$  decreases, and there is an associated increase in  $Q_d$  because of solute drag effect. However, it is also important to realize that there are limits on  $Q_d$  and  $\gamma_b$  related to reaching a metastable equilibrium when a certain grain size  $D^*$  is reached (when  $\gamma_b = 0$ ).

### 2.1. Thermodynamics of grain growth

The thermodynamics of grain growth is based on the concept that nanocrystalline materials can be stabilized against grain growth by GB segregation. This concept is related to the Gibbs adsorption equation and can be formally written as

$$\gamma_b = \gamma_0 - \Gamma_{b0} \left[ RT \ln \left( x_0 - \frac{3\Gamma_{b0}V_m}{D} \right) + \Delta H_{\text{seg}} \right], \quad (4)$$

where  $\gamma_0$  is the GB energy for the case of a pure material,  $V_m$  is the molar volume of the alloy,  $\Delta H_{\text{seg}}$  is the heat of segregation,  $\Gamma_{b0}$  is the saturated solute excess, and  $\Gamma_b$  is the solute excess at the boundary. Note that  $\Gamma_b$  is less than  $\Gamma_{b0}$  for the case where the GB is not saturated by solute and that these values are equal for the GB saturated case. The term  $\gamma_b$  is composed of 2 terms: the first reflects the GB energy in the absence of solute ( $\gamma_0$ ); and the second larger term modifies  $\gamma_b$  by accounting for the energy reduction caused by segregation of solute.

Chen et al. [24,45] have applied a first order Taylor expansion of Eq. (4) and an equation of mass conservation for nanocrystalline materials ( $\Gamma_{b0} = x_0\rho(D/6 + \delta)$ ) to obtain an expression for  $\gamma_0$  in

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