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Stability criteria for nanocrystalline alloys



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ABSTRACT

Alloying nanocrystalline materials to stabilize them against grain growth is proving a critical enabling strategy for the processing and usage of bulk nanocrystalline parts. Alloying elements that segregate strongly to grain boundaries can lead to a preference for nanocrystalline structure, and to be most stable the grain boundary segregated state would need to be preferred to forming any other phase or solute configuration, including a solid solution, ordered compounds, or solute precipitates. In this paper, a stability criterion is developed by comparing the enthalpy of the grain boundary segregated state against such stable bulk phases. This enthalpic criterion is also translated into a lattice model framework to enable the use of Monte Carlo simulations to incorporate entropic and geometric effects in assessing nanocrystalline stability. Monte Carlo simulations show that entropy can play a role in stabilizing nanocrystalline states, leading to duplex structures, and also in forming a grain boundary network preferentially over a disordered or amorphous-like bulk phase.

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1. Introduction

Achieving grain sizes on the nanometer length scale (<100 nm) leads to unique property combinations, both structural [1–5] and functional [6–8], due to the dominant presence of grain boundaries. This refinement is however accompanied by a large driving force for grain growth: doubling the grain size of a nanocrystalline material leads to a ~1000 times larger decrease in grain boundary area than does doubling a micron-scale grain size. This can cause rapid grain growth at relatively low homologous temperatures in nanocrystalline materials [9–12], which makes it difficult to produce bulk nanocrystalline parts and challenges their use in service.

One way to suppress this structural instability is to alter the energy landscape of the material through chemistry. Alloying can play two roles in shaping the energy landscape to increase resistance to grain growth: the alloying element can increase the energetic barrier (or activation energy) to grain growth through solute drag and/or Zener pinning, or it can decrease the energetic benefit of grain growth through grain boundary segregation according to the Gibbs adsorption isotherm [13–15]. In the latter case, Weissmüller showed that the driving force for grain growth can be eliminated if the energetic preference of grain boundary sites for

the solute is strong enough, as governed by the enthalpy of grain boundary segregation, ΔH_{seg} [13]. This route to stabilizing nanocrystalline materials has been gaining favor [1,16–33] as it can not only produce a more reliable form of stability but is also potentially easier to design for; due to its thermodynamic nature, achieving this stability mostly depends on choosing the right alloy combination.

The first alloy selection criterion to stabilize the nanocrystalline state was proposed by Weissmüller, based on the Gibbs adsorption isotherm [13]:

$$\Delta H_{\text{seg}} > \frac{\gamma}{T} - k_B T \ln(X) \quad (1)$$

The inequality states that the enthalpy of grain boundary segregation, ΔH_{seg} , must be large enough to overcome the enthalpic penalty of the grain boundary, γ/T (γ : pure solvent grain boundary energy; T : solute excess in the grain boundary), and the entropic advantage of a crystalline solid solution (k_B : Boltzmann's constant; T : temperature; X : intragranular solute concentration). While this equation only applies in the dilute limit, it has been extended using regular solution models, which produce more general forms of Eq. (1) [22–27]. When these criteria have been used to select stable alloy chemistries, the resulting nanocrystalline states are usually found to be stable at low homologous temperatures. However, when the temperature is increased, second phases often form at grain boundaries where the solute is enriched, as seen

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in Ni-P, Co-P, Fe-Zr and Ni-W [28–33]. Such precipitation is accompanied by subsequent grain growth when the grain boundaries are no longer sufficiently stabilized by solutes, which are instead precipitated in the second phase. Thus, stability against grain growth in such alloys is actually a form of metastability, and a deeper level of stability would be a nanocrystalline state in which grain boundary segregation is preferred over the formation of bulk phases.

A systematic way to study the stability of the grain boundary segregated state with respect to bulk solute-containing phases is to include the grain boundary segregated state on a bulk free energy diagram. Using regular solution models to describe the free energy of the segregated grain boundary as a function of global solute concentration, Murdoch and Schuh [23] developed criteria for stability of a grain boundary segregated state against both grain growth and second phase formation for positive enthalpy of mixing (ΔH_{mix}) systems using the form:

$$\Delta H_{\text{seg}} > c(\Delta H_{\text{mix}})^a \quad (2)$$

where the coefficients a and c depend on the homologous temperature and were fitted to the results of the regular solution model. For a given temperature, two sets of a and c describe stability: one specifies the criterion for metastability, where formation of a solute-rich phase is not considered, and the other, which has a larger c and therefore also a larger threshold value for ΔH_{seg} , specifies stability both against grain growth and phase separation. This same approach can be used to study stability against compound formation, as was done for Fe-Zr alloys by Zhou and Luo [24], but a general stability criterion for a grain boundary segregated state against compound formation has not yet been developed.

The reliability of the stability criterion in Eq. (2) is limited by the regular solution assumption, which assumes a random distribution of solute atoms along the grain boundary. This is a poor assumption; grain boundary segregation occurs largely because of the diversity of possible solute sites in a boundary, and solute is expected to populate such sites in decreasing order of energetic relief. Solute ordering is not only expected, but routinely observed in grain boundary segregation [34–40]. In order to relieve regular solution assumptions, Chookajorn and Schuh developed a lattice-based Monte Carlo approach that considers both bulk and nanocrystalline configurations within its phase space and determines the free-energy minimizing microstructure [41]. Because this simulation no longer constrains the possible equilibrium states to either be a bulk state or a segregated nanocrystalline state, it is a powerful tool for studying the equilibria of strongly grain boundary segregating alloys. One such observation was the existence of a duplex nanostructure wherein solute-rich precipitates form alongside solute segregated grain boundaries, which is difficult to consider analytically [41,42]. They also used their model to develop stability criteria:

$$\text{Metastability } \Delta H_{\text{seg}} > \frac{1}{2}\Delta H_{\text{mix}} + k\gamma \quad (3)$$

$$\text{Stability } \Delta H_{\text{seg}} > \Delta H_{\text{mix}} + k\gamma \quad (4)$$

where γ is the grain boundary energy of the pure solvent and k is a scaling factor used to estimate the grain boundary area per atom (approximated in that work as the atomic volume of solvent divided by the grain boundary thickness [22]). This stability criterion conforms to physical intuition about the energy relationship necessary for stability in a positive enthalpy of mixing system: in order for the grain boundary segregated state to be the lowest

energy configuration, it must reduce the energy enough to offset both the energy penalty of forming a grain boundary ($k\gamma$) and the energy benefit of forming a solute-rich precipitate (ΔH_{mix}). Note that these criteria consider enthalpic preference only, because the Monte Carlo method was used to handle configurational entropy. To complete the analogy of these expressions with Eq. (1) would require the addition of an entropy term (e.g. $k_B T \ln(X)$).

The criteria in Eqs. (3) and (4) were developed only for alloys with positive enthalpies of mixing, and further tacitly assuming that the enthalpy of the grain boundary segregated state is well-represented by the solute-solvent atom interaction energy at a grain boundary. While these criteria present an interesting advance, the number of alloy systems with a positive enthalpy of mixing is small: considering transition metal pairs, roughly 40% have a positive enthalpy of mixing whereas 60% have a negative one and/or form intermetallic compounds [43]. Furthermore, the most widely studied and/or commercially successful grain-boundary segregating systems are compound formers (i.e., Ni-W, Ni-P, Co-P, Fe-Zr). There is therefore a need to extend the stability criteria to non-regular systems with negative enthalpies of mixing, and our purpose in this paper is to do so. By more rigorously considering the ordered configuration of solute at the grain boundaries and the effect of ordered compounds, we first develop an analytical criterion and subsequently cast it into lattice model terms in order to inform Monte Carlo explorations of nanocrystalline stability.

2. Stability criterion from enthalpic considerations

Grain boundary segregation, like precipitation, is largely believed to be an enthalpic effect, and is thus a form of chemical ordering. The competition between different ordered states can be resolved by determining which ordered state provides the lowest enthalpy for the alloy system, as is typically done for ordered compounds in developing 0 K phase diagrams [43–45]. The energies of ordered states as a function of composition can be compared on an energy diagram such as Fig. 1 to determine regimes of stability, where here we particularly focus on solute-lean compositions without loss of generality. The enthalpy of the binary alloy system with an ordered phase, H_{ord} , can generally be written as:

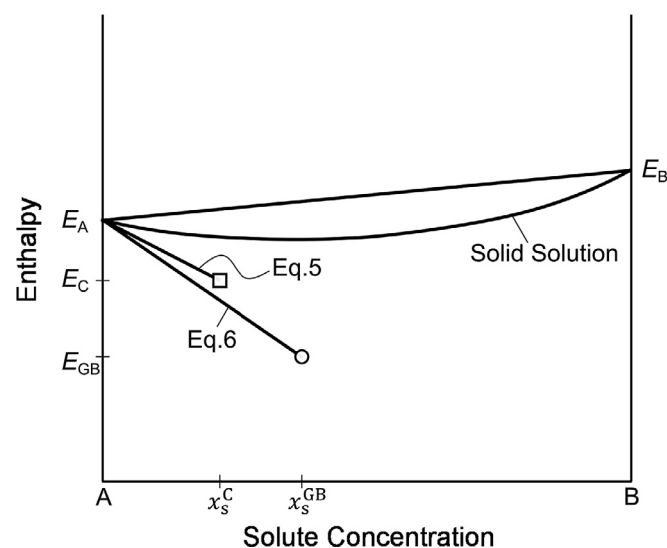


Fig. 1. Schematic of the binary alloy energy diagram including an ordered phase (square) and a 2D grain boundary compound (circle) where the energy of non-stoichiometric compositions is calculated by the lever rule (lines).

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