Optimization strategies for identifying the controlling mechanism for solid-state transformation in FeCrNi during rapid solidification

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Abstract. Retained free energy drives the transformation from metastable to stable phase during double recalescence of steel alloys. Statistical methods were used to identify the mechanism controlling cluster growth based on the principle of microstructural reversibility. Application of the coefficient of determination during optimization procedures showed that an extrinsic mechanism controls nucleation and that negligible healing occurs such that retained free energy from primary phase undercooling and melt convection enhance secondary nucleation.

1. Background
Double recalescence during rapid solidification involves nucleation of a metastable phase from the undercooled melt with subsequent transformation to the stable phase; both processes involve a rapid increase in temperature and the incubation time, or delay between these events, is a strong function of both undercooling and convection [1-3] for FeCrNi alloys. Previous work has shown that nucleation of the stable fcc austenite phase occurs along subgrain boundaries within the pre-existing metastable bcc ferrite phase and that the cluster geometry is of the form of two opposing hemispherical caps [4, 5] sharing a border that straddles the grain boundary (GB).

From classical nucleation theory the free energy change due to addition of an atom to the cluster of volume V and radius r is composed of positive terms hindering the transformation associated with the required creation of new surface, with a surface energy penalty of γ, and negative terms driving the transformation associated with reduction of volume free energy ΔGv ≡ ΔGt. The wetting angle θ is defined by a surface energy balance along the circular edge where the two caps meet such that

$$\cos \theta = \frac{\gamma_{MM}}{2\gamma_{MS}}$$

$$f(\theta) = \frac{1}{2} (1 - \cos \theta)^2 (2 + \cos \theta)$$

$$r^* = \frac{2\gamma_{MS}}{\Delta G_v}$$

The surface energy terms are strong functions of defect concentration [6] and thus the wetting angle seen during nucleation of the second phase may be influenced by conditions which occur during formation of the first. This effect can be quantified for solid-solid transformations where double recalescence is observed using the theory of retained free energy [7] where the system volume free energy is composed of two terms – the first driven by undercooling set by the equilibrium phase diagram ΔGv and the second from damage retained from primary solidification ΔGD. This second term is also composed of two terms – one describing retained free energy from primary undercooling ΔGm and the other describing retained free energy due to convection during primary solidification ΔGC.
The retention free energy may be reduced by some empirical fraction $f$, representing healing of the retained damage through processes such as dynamic recrystallization or relaxation.

For the dual cap geometry the new surface area that must be formed is composed of two abutting hemispherical sections with area $A_{M/S}$ while the surface that is destroyed is the circular interface where they meet $A_{M/M}$. Subscripts refer to metastable ($M$) and stable ($S$) phase, respectively.

$$
\Delta G = \Delta A_{M/S} \gamma_{M/S} - \Delta A_{M/M} \gamma_{M/M} - \nabla \Delta G_f = 4\pi \left(r^2 \gamma_{M/S} - \frac{r^3}{3} \Delta G_f \right) f (\theta)
$$

(4)

The incubation time is evaluated based on the principle of microstructural reversibility as described by Feder et al. \cite{8} where a cluster is assumed to be able to grow at the same rate as it would decompose:

$$
\tau = -\frac{4k_b T}{\beta \left( \frac{\partial^2 \Delta G}{\partial n^2} \right)}
$$

(5)

Other authors have developed models which result in equations of similar form \cite{9-15} with the only difference being the initial constant. In all these equations the key parameters are the atomic attachment rate from the parent phase to the cluster $\beta$ and the curvature of the free energy curve with respect to addition of an atom to the cluster.

The purpose of this paper is to develop a strategy to investigate the sensitivity of potential statistical criteria to optimize the decision process and determine which mechanism controls cluster growth for a given alloy. The approach is to compare how well the observed data fits model predictions using two statistical quantities – the coefficient of determination \cite{16} $R^2$ and the Pearson product-moment correlation coefficient \cite{17} $r$:

$$
R^2 = 1 - \frac{\sum(y_i - f_i)^2}{\sum(y_i - \bar{y})^2}
$$

(6)

$$
R = \sqrt{\frac{\sum(x_i \cdot y_i) - \frac{\sum x_i \cdot \sum y_i}{n}}{\sqrt{\sum x_i^2 - \frac{\sum x_i^2}{n}} \cdot \sqrt{\sum y_i^2 - \frac{\sum y_i^2}{n}}}}
$$

(7)

In these equations the subscript $i$ on the dependent variable $y$ and independent variable $x$ represent observed individual events to be compared to corresponding model prediction behavior using the dependent variable $f$. The coefficient of determination is the proportion of the variance in $y$ that is predicted from $x$. The Pearson correlation coefficient quantifies the strength of the linearity of a relationship between two sets of data. Note that the value obtained by linear regression using a widely-used commercial statistical package commonly employed by personal computer users labels the regression fit as an $R^2$-value but actually displays the correlation coefficient $r$. The goal of this paper is thus to identify a robust and unbiased method to optimize evaluation of the limiting cluster growth mechanism and from that gain insight on how cluster growth proceeds.

2. Transformation mechanisms

In order to develop an equation to predict the delay time given the melt condition, the principle of microstructural reversibility requires definition of the two key parameters identified in Equation 5.

From classical nucleation theory the curvature can readily be obtained by differentiation of Equation 4 twice. Since this relationship is a function of cluster radius and the differentiation is to be done relative to an incremental change in number of atoms the process requires a simple substitution based on:

$$
V = \frac{4}{3} \pi r^3 f (\theta) \frac{n \Omega}{N_A} = \frac{4}{3} \pi r^3 f (\theta) \frac{N_A}{\Omega}
$$

(8)

$$
\frac{\partial \Delta G}{\partial n} \frac{\partial \Delta G}{\partial r} \frac{\partial n}{\partial r} \frac{\Omega}{N_A} \left(2\gamma_{M/S} \right) \frac{\partial \Delta G}{\partial r} \frac{\partial n}{\partial r} = \frac{\partial \Delta G}{\partial r} \frac{\partial n}{\partial r} \frac{\Omega}{N_A} \left(2\gamma_{M/S} \right) \frac{\partial \Delta G}{\partial r} \frac{\partial n}{\partial r}
$$

(9)
\[
\frac{\partial^3 \Delta G}{\partial n^3} = d \left( \frac{\partial \Delta G}{\partial n} \right) / \partial r = -\frac{\gamma_{MS}}{2\pi r^2 f(\theta)} \frac{\Omega_2}{N_A} \frac{\partial^3 \Delta G}{\partial n^2} = -\frac{\Delta G_s^4 \Omega_2^2}{32\pi \gamma_{MS}^2 f(\theta) N_A^2}
\]

Note that this value is negative since the curvature is evaluated at the local maximum in the free energy curve such that the cluster is stable with addition of extra atoms. Thus the negative sign in Equation 5.

The result of this calculation is that the curvature is inversely proportional to the radius raised to the 4th power. With substitution for an evaluation of the critical cluster radius shown in Equation 1, where the radius is inversely proportional to free energy, the curvature becomes proportional to \((\Delta G_s)^4\).

The attachment rate \(\beta\) is a strong function of selection of the mechanism controlling cluster growth. If mass transfer through diffusion is the limiting step, the attachment rate will be proportional to the interfacial mass transfer area. Doubling the area results in twice the number of atoms attaching per unit time, halving the delay time. Since the interfacial area is some function of the cluster radius then the delay time will be a unique function of the transfer geometry. If mass transfer is not the rate limiting step for cluster growth and if some extrinsic influence, such as matrix strain or mobility of dislocations to the cluster to modify the wetting angle and augment interface potency [6], then the attachment rate is independent of \(r\). These relationships are presented in Table I.

| Limiting mechanism          | Attachment rate                                 | Delay time |
|-----------------------------|--------------------------------------------------|------------|
| Bulk diffusion attachment   | \(\beta \propto A_s = 4\pi r^2 (1 - \cos \theta)\) | \(\tau \propto \Delta G_s^{-2}\) |
| GB diffusion attachment     | \(\beta \propto A_s = \delta (2\pi r \sin \theta)\) | \(\tau \propto \Delta G_s^{-3}\) |
| Extrinsic factor limited    | \(\beta \propto \text{constant}\)                | \(\tau \propto \Delta G_s^{-4}\) |

If diffusion through the bulk controls, the transport area is the hemispherical cap surface which is proportional to \(r^2\). If diffusion through the grain boundary controls, the area is the circumference of the basal plane multiplied by the grain boundary thickness \(\delta\) which is proportional to \(r\). If mass transfer is not the rate limiting step for cluster growth and if some extrinsic influence, such as matrix strain or mobility of dislocations to the cluster, then the attachment rate is independent of \(r\). Combining this result with Equation 10 and eliminating \(r\) using Equation 1 yields the functional relationship between delay time and volume free energy. The extrinsic mechanism is functionally equivalent in form \(\tau \propto \Delta G_s^{-4}\) to other previous models [9-13] and has been verified through simulation [18] and experiment [19] although the assumptions during development of the previous work were different than in the current study. The bulk mechanism is functionally similar to Shao and Tsakiropoulos [20] with the form \(\tau \propto \Delta G_s^{-2}\).

### 3. Experimental results

Results from levitation experiments have been presented previously for no-flow conditions using electrostatic levitation (E SL), laminar Marangoni flow using ESL with laser heating (ESL-L), transitional and turbulent flow using space electrostatic levitation (ISS-EML) and fully turbulent flow using ground-based electromagnetic levitation (EML).

Details of the experimental techniques are available in the literature [3, 7] based on an evaluation of the observed delay times for a 60Fe20Cr20Ni (wt%) alloy as a function of undercooling and melt convection. Melt shear was calculated in the same manner as presented by Lee et al. [21] adjusted for the thermophysical properties of the steel alloy using magnetohydrodynamic modelling.

### 4. Statistical optimization

The following analysis quantifies the performance of the three candidate attachment controlling mechanisms using the two statistical criteria described in Equations 6 and 7. Using these techniques, an evaluation is conducted to determine which mechanism is statistically most likely to control the delay behavior and determine the fraction of retained free energy \(f_t\) that contributes to the transformation total driving force \(\Delta G_T\). Alloy properties are documented in the literature supplemental material.
A dimensionless technique\cite{1} was used to compare statistical approaches. The reference state was for the thermodynamically-limiting condition defined by the equilibrium phase diagram. For double recalescence to occur the undercooling must be sufficient to access the metastable phase corresponding to a melt temperature at or below the metastable liquidus. This is the smallest undercooling that can result in formation of the metastable phase and defines the minimum total free energy possible, in the absence of melt stirring with $\Delta G_D = \Delta G_M = \Delta G_C = 0$, such that $\Delta G_R = \Delta G_T = \Delta G_s$. This results in the longest possible delay time $\tau_R$. From this condition the observed delay time defines a dimensionless delay time ratio $N_t$ and the corresponding undercooling defines a dimensionless driving force ratio $N_M$.

\[
N_t = \frac{\tau_{\text{exp}}}{\tau_R}, \quad N_M = \frac{\Delta G_r}{\Delta G_s} \quad (11)
\]

These two independent quantities are shown in Figure 1 where the results for bulk diffusion attachment (gray line) and extrinsic limited mechanisms (black line) are displayed. The grain boundary attachment curve lies between these and is not shown for clarity. Filled triangles are ESL, open triangles are ESL-L, open diamonds are ISS-EML and filled diamonds are EML. The slopes agree well with theoretical values and a linear regression of the data results in slopes of $m_{\text{bulk}} = -1.994 \pm 0.032$, $m_{\text{GB}} = -3.008 \pm 0.029$, and $m_{\text{ext}} = -4.016 \pm 0.032$. Of particular interest is the inability of the $D_{\text{bulk}}$ and $D_{\text{GB}}$ mechanisms to describe behavior of highly stirred experiments using EML; the data does not follow the regression well and shows systematic deviation not observed for the extrinsic mechanism. This systematic deviation can easily be seen by looking at the trend for any given symbol type. In particular, the filled-diamond shape using EML at high dimensionless driving force for the $D_{\text{bulk}}$ mechanism shows negative deviation at high driving force and positive deviation as the driving force is reduced. The behavior for the Extrinsic mechanism consistently follows the theoretical curve over the entire range. Similar behavior is seen for the filled triangles from ESL and open triangles from ESL-L testing.

Figure 1 – Dimensionless predictions

This is further emphasized in Figure 2 where the predicted delay is compared to the observed delay. The solid black line with predictions from the extrinsic model shows a consistently better fit to both
ESL (zero melt shear) and EML (high shear) experimental data as compared to the dotted line $D_{\text{bulk}}$ mechanism predictions.

![Figure 2 – Experimental data comparison](image)

These trends are also evident when observing the statistical measures of fit. Figure 3 presents the optimized coefficient of determination as a function of the fraction of retained free energy over the range $0.5 < f_c < 1.0$. The best fit (highest $R^2$) occurs in all cases for $f_c > 0.9$ which implies that no healing
occurs and all free energy from metastable solidification is retained to augment stable phase nucleation. Furthermore, the extrinsic mechanism outperforms both the grain boundary and bulk mechanisms as previously discussed – except for $f_x \to 1$ where $R_{\text{max}}^2$ is 0.948 and 0.946 for extrinsic and grain boundary mechanisms respectively and thus differences are not statistically significant. The method is robust and trends are plainly evident because $R^2$ drops off significantly indicating that the measurement sensitivity is high. In comparison the dotted line represents the optimized correlation coefficient for the identical conditions. Not only is deviation nearly identical for all three mechanisms but the fidelity of the result limits the ability to define how $f_x$ influences model performance. Use of the $r$-value is not recommended.

5. Conclusions
Optimization strategies were compared to define the mechanism that controls cluster growth during nucleation of the stable phase within a pre-existing metastable solid. The coefficient of determination outperforms the correlation coefficient. Extrinsic factors appear to control nucleation rather than either bulk or grain boundary diffusion. The empirical parameter describing the fraction of free energy that is retained has been evaluated for the FeCrNi system and found to indicate that free energy is fully retained following primary recalescence such that $f_x \to 1$ and the added energy promotes enhanced nucleation of the second phase. The dimensionless technique provides insight into the dynamics of this process.

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## Nomenclature

| Symbol  | Units | Definition                                                                 |
|---------|-------|---------------------------------------------------------------------------|
| $A$     | (m$^2$) | area                                                                       |
| $D_{\text{bulk}}$ | ( - ) | bulk diffusion-controlled mechanism                                        |
| $D_{\text{GB}}$ | ( - ) | grain boundary diffusion-controlled mechanism                               |
| $\text{EXT}$ | ( - ) | extrinsically-controlled mechanism                                         |
| $f_i$   | ( - ) | model prediction using the dependent variable                             |
| $f(\theta)$ | ( - ) | cluster geometry factor                                                   |
| $f_r$   | ( - ) | fraction of damage which is retained (not healed) before recalescence      |
| $\Delta G$ | (J/m$^3$) | free energy                                                               |
| $\Delta G_m$ | (J/m$^3$) | free energy due to undercooling relative to the metastable phase          |
| $\Delta G_s$ | (J/m$^3$) | free energy due to undercooling relative to the stable phase              |
| $\Delta H$ | (J/mol) | enthalpy                                                                   |
| $k_B$   | (J/atom$\cdot$K) | Boltzmann constant                                                        |
| $m_{\text{bulk}}$ | ( - ) | slope of the regression for bulk model                                    |
| $m_{\text{GB}}$ | ( - ) | slope of the regression for grain boundary model                           |
| $m_{\text{ext}}$ | ( - ) | slope of the regression for extrinsic model                               |
| $n$     | (atoms) | number of atoms in a cluster                                               |
| $n_i$   | ( - ) | number of observed events                                                 |
| $N_A$   | (atom/mole) | Avagadro’s number                                                         |
| $N_{\text{dr}}$ | ( - ) | dimensionless driving force ration obtained from observed undercooling   |
| $N_t$   | ( - ) | dimensionless delay time ratio obtained from observed incubation time     |
| $r$     | (m) | radius, with * for critical cluster radius                                |
| $\tau$ | (s) | theoretical incubation delay time                                          |
| $\tau_{\text{EXP}}$ | (s) | experimentally observed incubation delay time                             |
| $\theta$ | (radians) | wetting angle                                                              |
| $\Omega$ | (m$^3$/mol) | atomic volume                                                             |
| $\beta$ | (atoms/s) | atomic attachment rate                                                    |
| $\gamma$ | (J/m$^2$) | surface free energy                                                       |
| $\dot{\gamma}$ | (s$^{-1}$) | rate of shear in liquid due to forced convection                           |
| $\Delta h$ | (J/s/m$^3$) | intercept for correlation of influence of convection on free energy       |
| $\Delta s$ | (J/s/m$^3$) | slope for correlation of influence of convection on free energy            |
| $c$     | ( - ) | convection damage                                                         |
| $D$     | ( - ) | total damage                                                              |
| $i$     | ( - ) | individual observed event                                                 |
| $m$     | ( - ) | metastable phase                                                          |
| $M/M$   | ( - ) | Metastable-metastable phase interface                                      |
| $M/S$   | ( - ) | Metastable-stable phase interface                                          |
| $R$     | ( - ) | reference value                                                           |
| $s$     | ( - ) | stable phase                                                              |
| $T$     | ( - ) | total                                                                     |
| $v$     | ( - ) | volume                                                                    |

## Subscripts

- $c$: convection damage
- $D$: total damage
- $i$: individual observed event
- $m$: metastable phase
- $M/M$: Metastable-metastable phase interface
- $M/S$: Metastable-stable phase interface
- $R$: reference value
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- $T$: total
- $v$: volume