Trans-Interface Diffusion Controlled Coarsening

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TMS 2005 Annual Meeting, John Morral Symposium
San Francisco, CA, February 14, 2005

Outline

- Brief review of the major predictions of the LSW theory.

- Illustration of how data on coarsening of γ'-type (Ni_3X) precipitates in binary Ni-X alloys (X = Al, Ga, Ge, Si, Ti) is utterly at odds with predictions of theory.

- For a variety of reasons we are investigating the morphological evolution and kinetics of coarsening of γ (Ni-Al solid solution) precipitates in a γ' (Ni_3Al) matrix. We call this the INVERSE alloy.

- As we will see, results on the inverse Ni-Al alloy prompted the development of the theory of Trans-Interface-Diffusion-Controlled (TIDC) coarsening.

- What is good about the TIDC theory, what needs work, and some directions for the future.

Part 1

LSW theory; effect of volume fraction; what's wrong!!!

Main Predictions of the LSW Theory

$$\langle r \rangle^3 - \langle r_o \rangle^3 = kt$$

$\langle r \rangle$ is the average particle radius at time t and $\langle r_o \rangle$ is its initial value.
The rate constant k is given by the equation

$$k \approx k(0) = \frac{8 D \sigma v_{m\gamma'}}{9 G''_m \, X_e^2}$$

$$\Delta X_e = X_{\gamma'e} - X_{\gamma e} \qquad\qquad G''_m = \left. \frac{d^2 G_m}{dX^2} \right|_{X_e}$$

$X_{\gamma e}$ and $X_{\gamma'e}$ are the equilibrium solubilities of Al in the γ and γ' phases
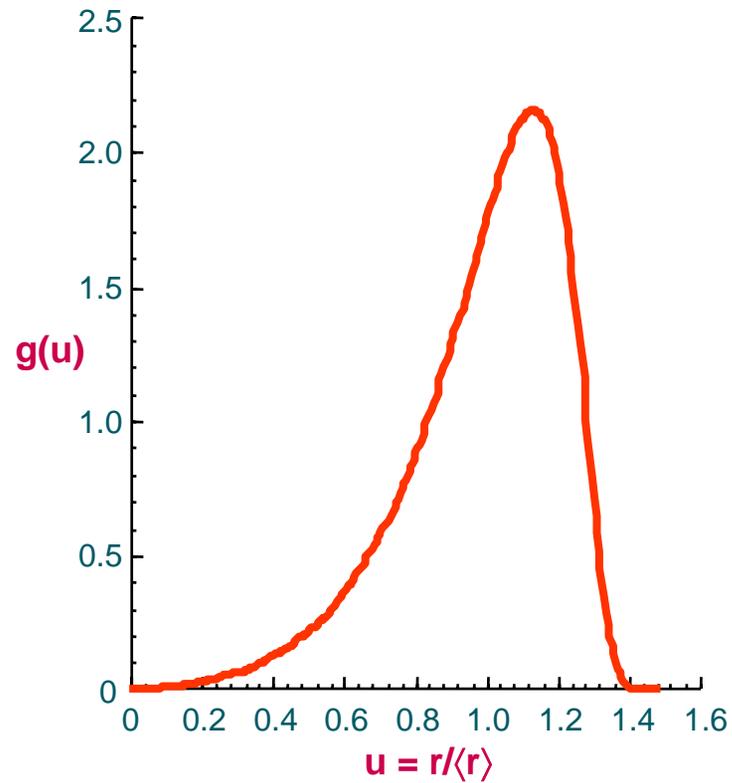$v_{m\gamma'}$ is the partial molar volume of solute in the γ' phase
D is the chemical diffusion coefficient
σ is the interfacial free energy
$G_{m\gamma}$ is the Gibbs free energy of mixing of the γ phase

SCALED DISTRIBUTION OF PARTICLE SIZES

$$g(u) = \frac{4u^2}{9}\left(\frac{3}{3+u}\right)^{7/3}\left(\frac{-3/2}{u-3/2}\right)^{11/3} exp\left(\frac{u}{u-3/2}\right); \quad u \quad 3/2$$

VARIATION OF SOLUTE CONCENTRATION WITH AGING TIME

$$X_\gamma - X_{\gamma e} = (\kappa t)^{-1/3}$$
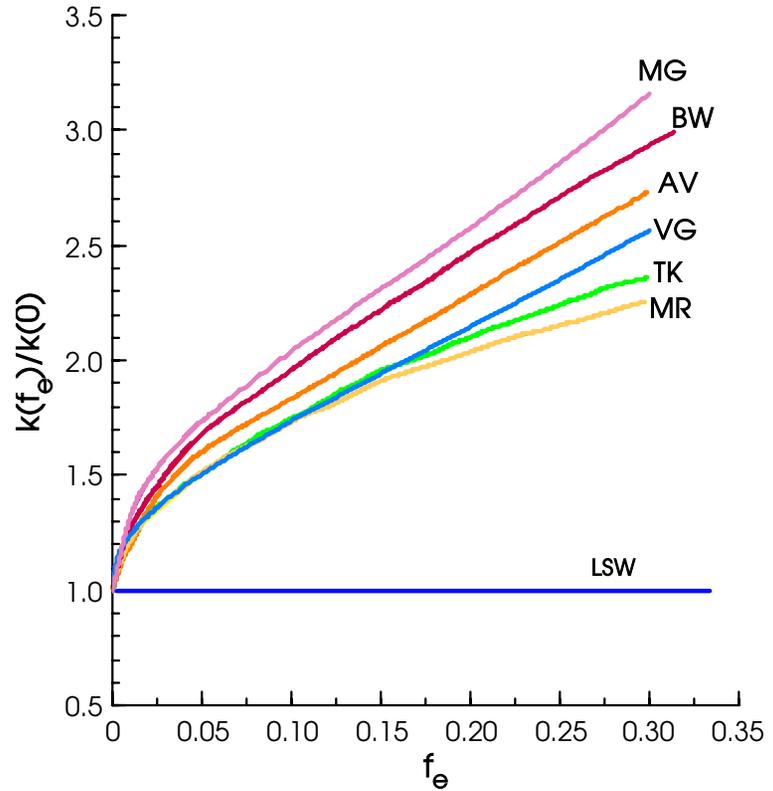
$$\frac{k}{\ell_c^3}$$

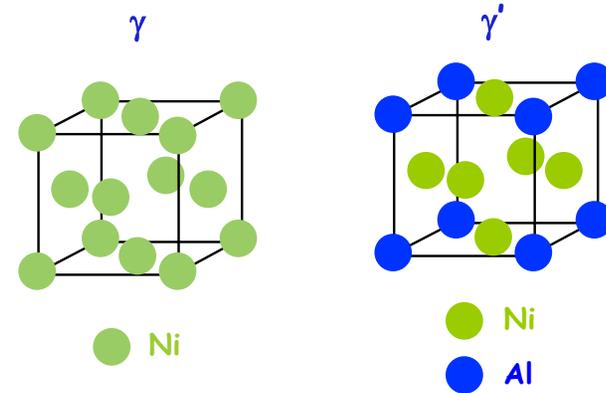Where ℓ_c is the capillary length, given by the equation

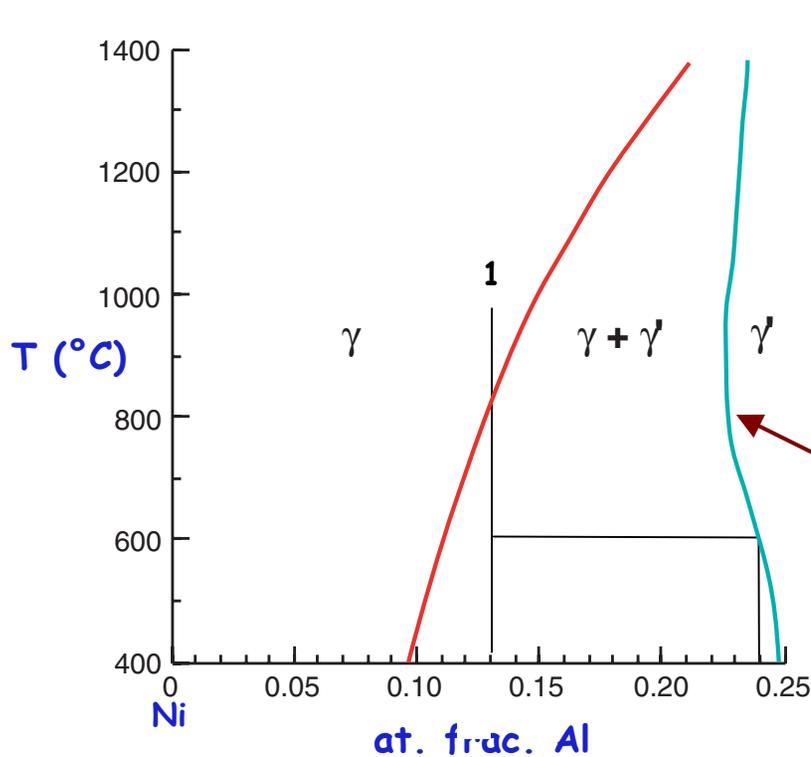$$l_c \quad \frac{2\, v_m{}'}{X_e G_m{}''}$$

Theoretically predicted dependencies on f_e of the rate constants for coarsening

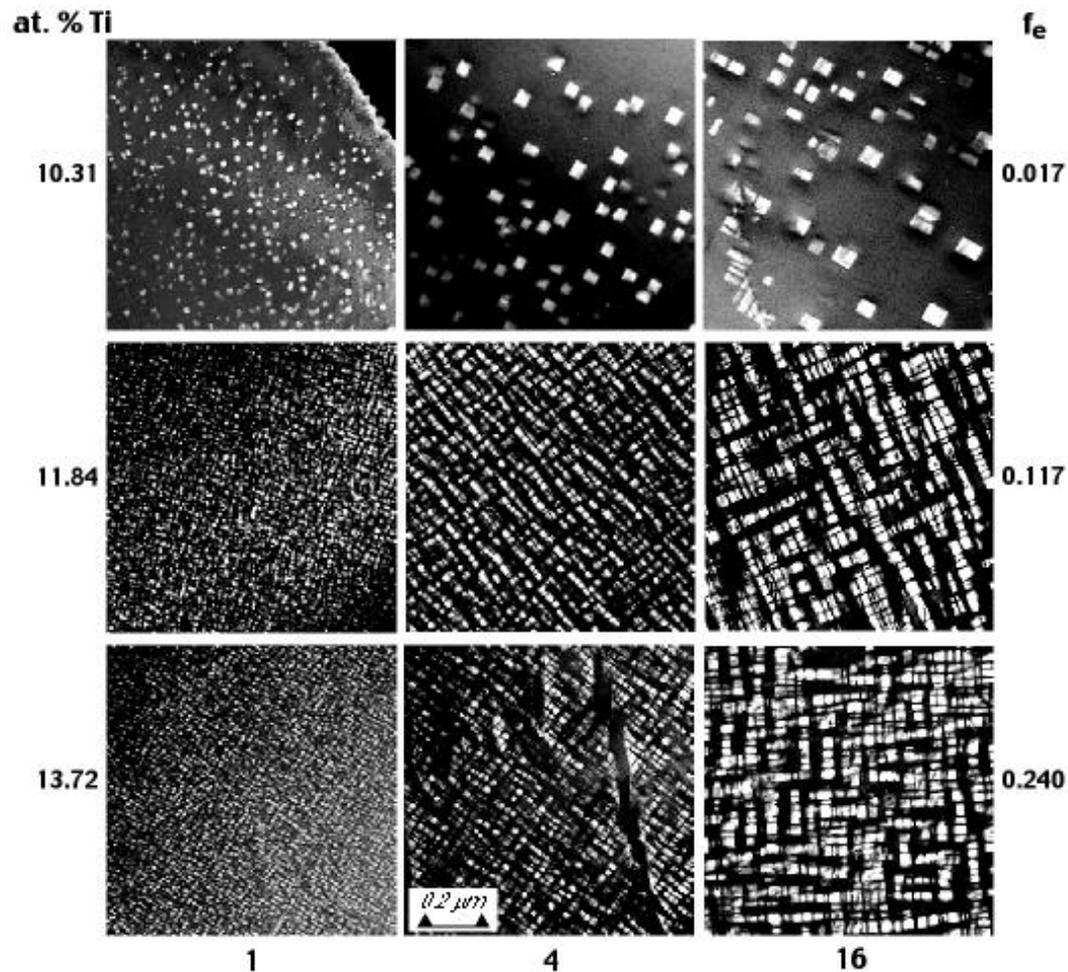$$\langle r \rangle^3 - \langle r_o \rangle^3 \;=\; k(f_e)t$$

Typical aging experiment for a "normal" Ni-Al alloy

Except for the shape of the (γ + γ')/γ phase boundary, we can substitute Ga, Ge, Si and Ti in this phase diagram

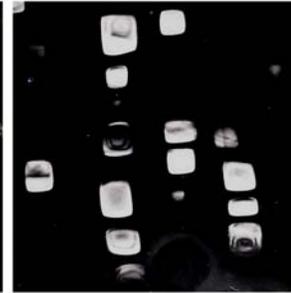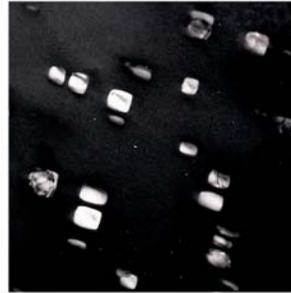**Ni₃Ti precipitates in Ni–Ti alloys aged at 720 °C for the times (in h) indicated**
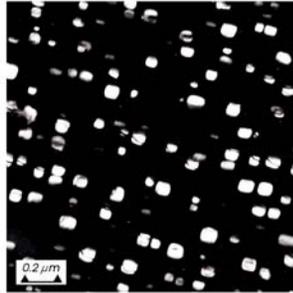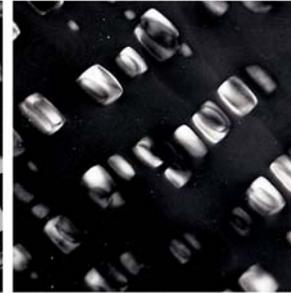
Dongman Kim
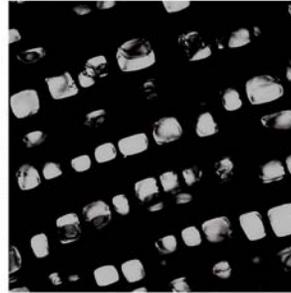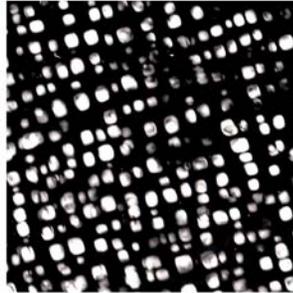
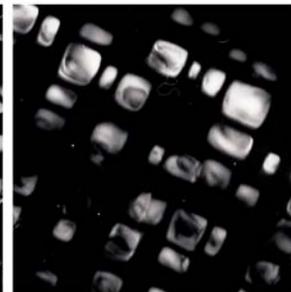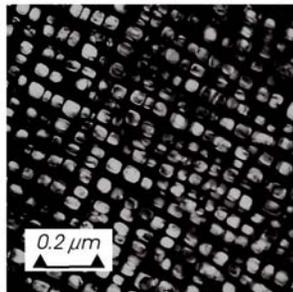at. % Ge — 12.15 · 13.02 · 14.03 ; f_e — 0.021 · 0.104 · 0.201 ; times (h): 1, 8, 16

Ni-Ge alloys aged at 724 °C for the times (h) indicated.

D.M. Kim and A.J. Ardell, *Acta Mater.* 51 (2003) 4073.

Ni₃Si in Ni-Si alloys aged at 650 °C
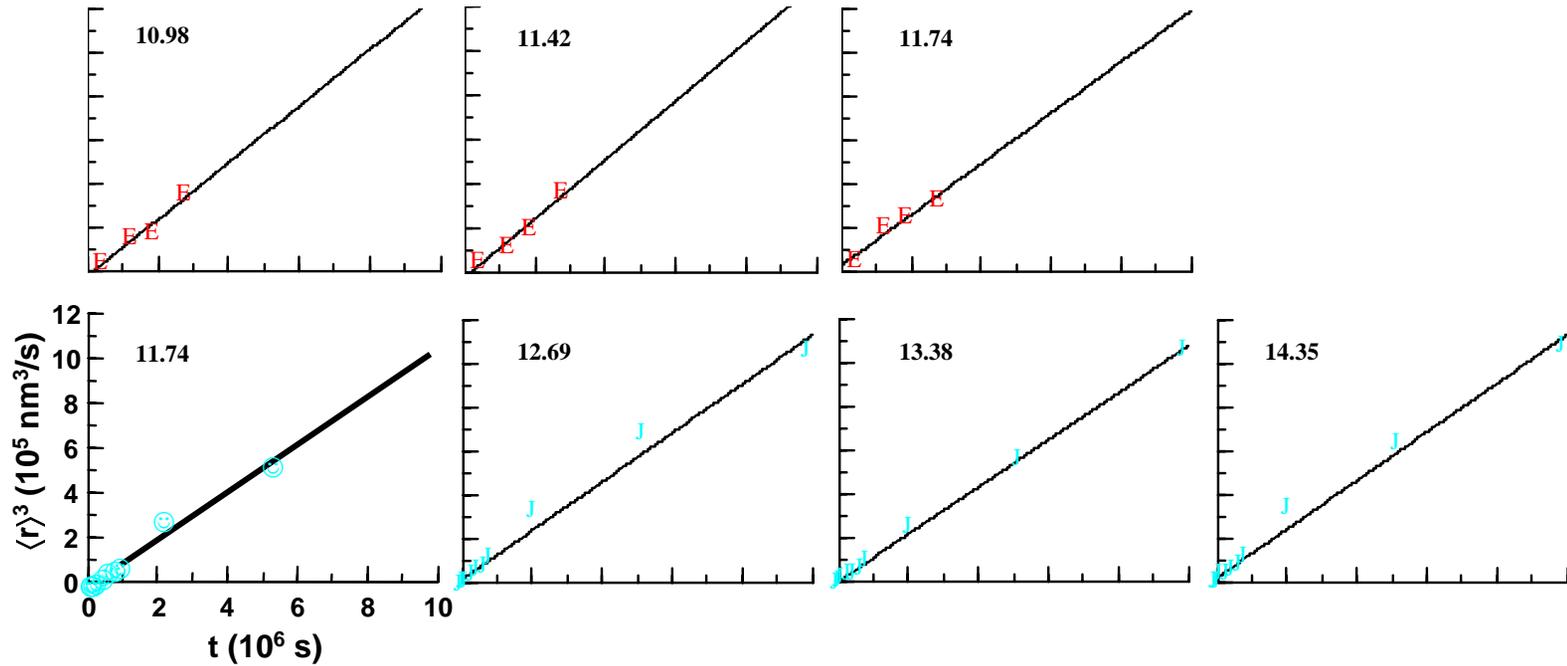
J.-H. Cho and A.J. Ardell, *Acta Mater.* **45** (1997) 1393.

Dependence on volume fraction of the rate constants for coarsening of Ni₃Si precipitates in Ni-Si alloys
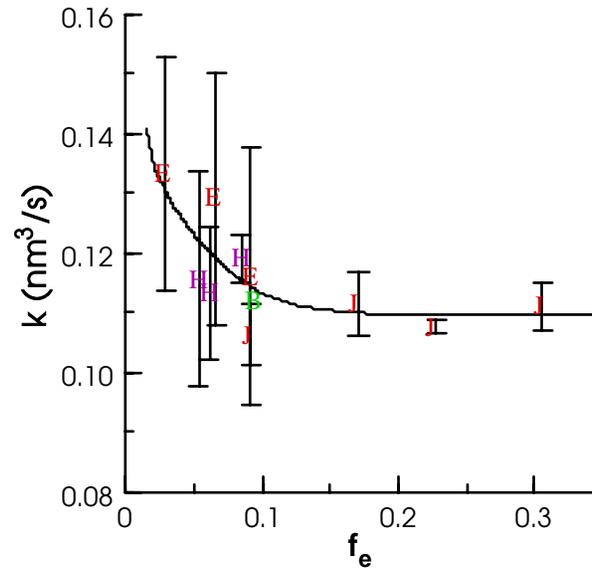
E This work (seeded/reaged)
J Cho and Ardell [6]
B Sauthoff & Kahlweit [10]
H Meshkinpour & Ardell [9]

J.-H. Cho and A.J. Ardell, *Acta Mater.* 46 (1998) 5907.

Dependence on volume fraction of the rate constants for coarsening of Ni_3Al precipitates in Ni-Al alloys

Dependence on volume fraction of the rate constants for coarsening of Ni_3Ti precipitates in Ni-Ti alloys
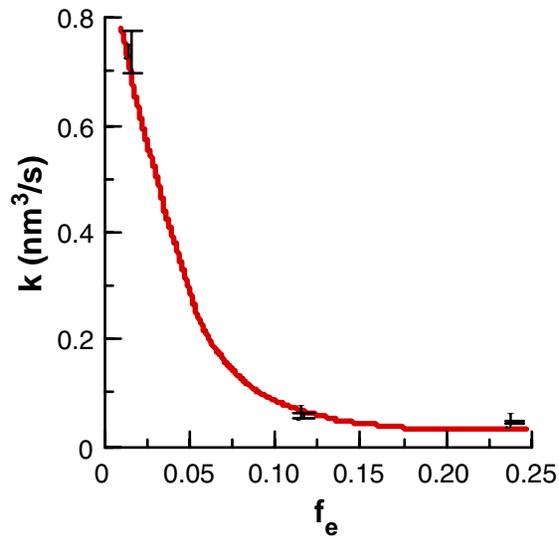
D.M. Kim and A.J. Ardell, *Scripta Mater.* 43 (2000) 381.

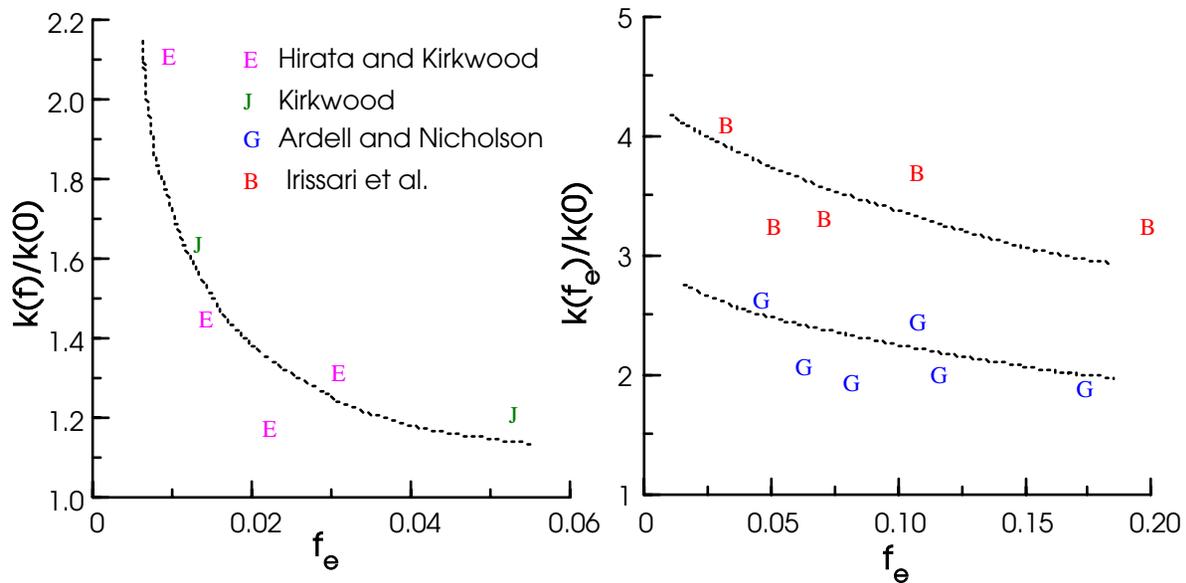# Dependence on volume fraction of the rate constants for coarsening of Ni_3Ge precipitates in Ni-Ge alloys
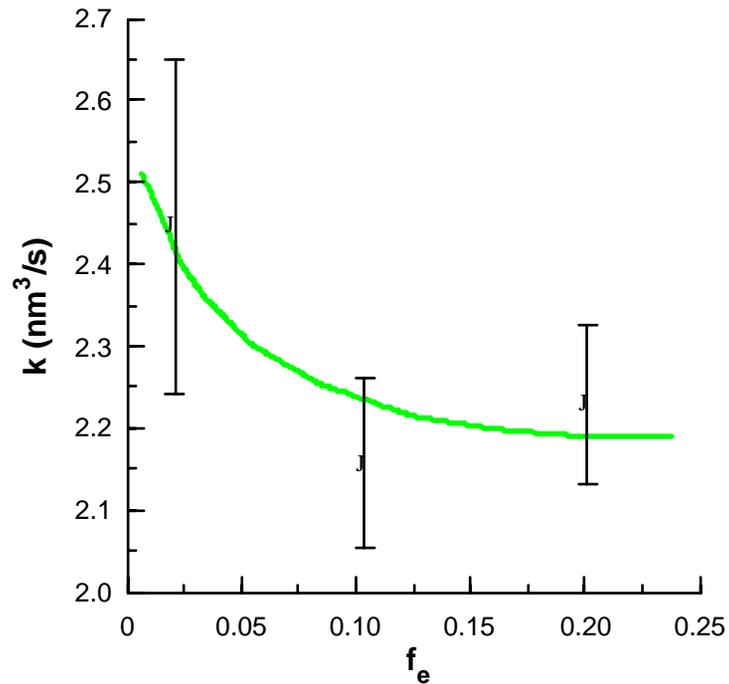
Part 1 summary

There is no doubt that the dependence of $k(f_e)$ on f_e is ANOMALOUS!!! It *decreases* with increasing f_e when f_e is small (≈ 0.08 or so), and remains nearly constant thereafter.

There is no acceptable explanation for the absence of an effect of volume fraction at the larger values of f_e.

Part 2

Results on the INVERSE alloy, i.e. coarsening of the Ni-Al solid solution phase (γ) from supersaturated Ni$_3$Al (γ')

Typical aging experiment for an "inverse" Ni-Al alloy
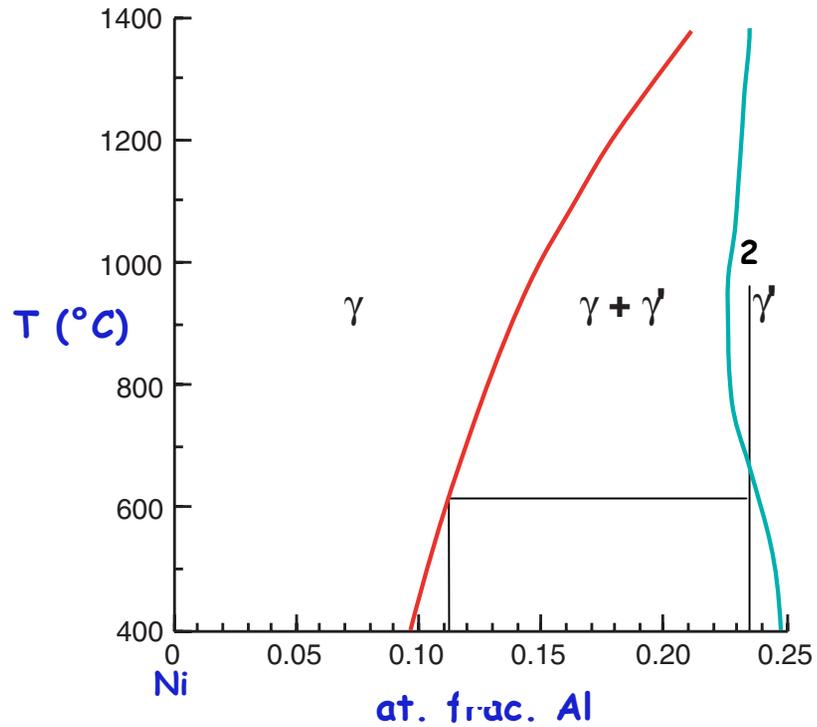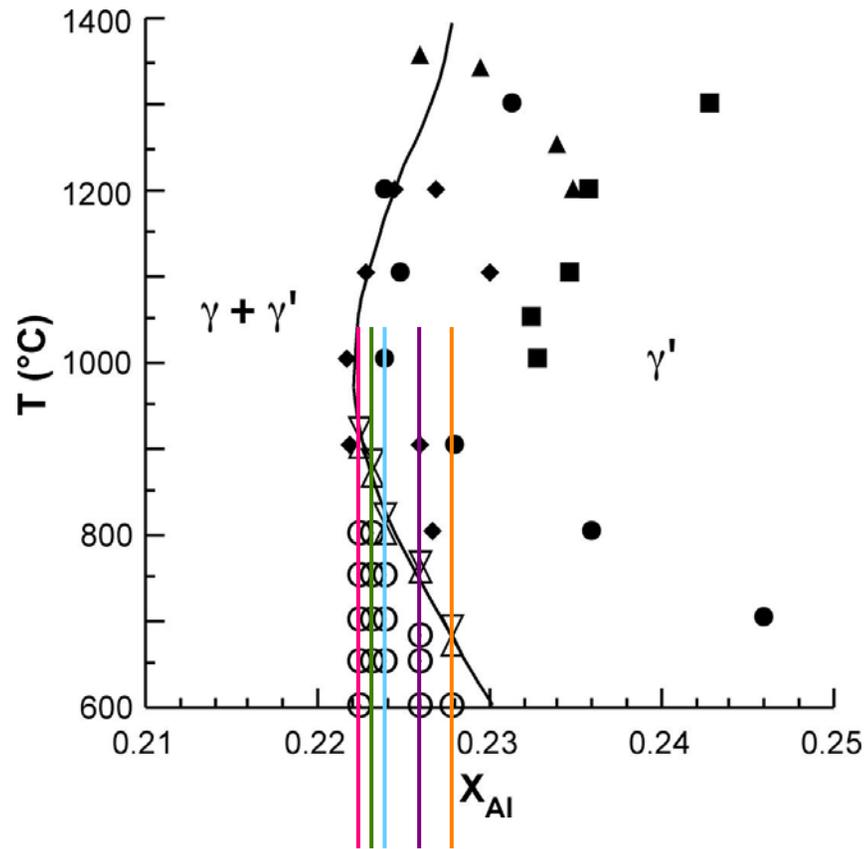
Y. Ma and A.J. Ardell, "The (γ + γ')/γ' phase boundary in the Ni–Al phase diagram from 600 to 1200 °C", Zeit. für Metallkunde <u>94</u> (2003) 972.

at.% Al

				f_e
22.60				0.025
22.40				0.042
22.33				0.048
22.25				0.055

200 nm

240   480   720   1824 h
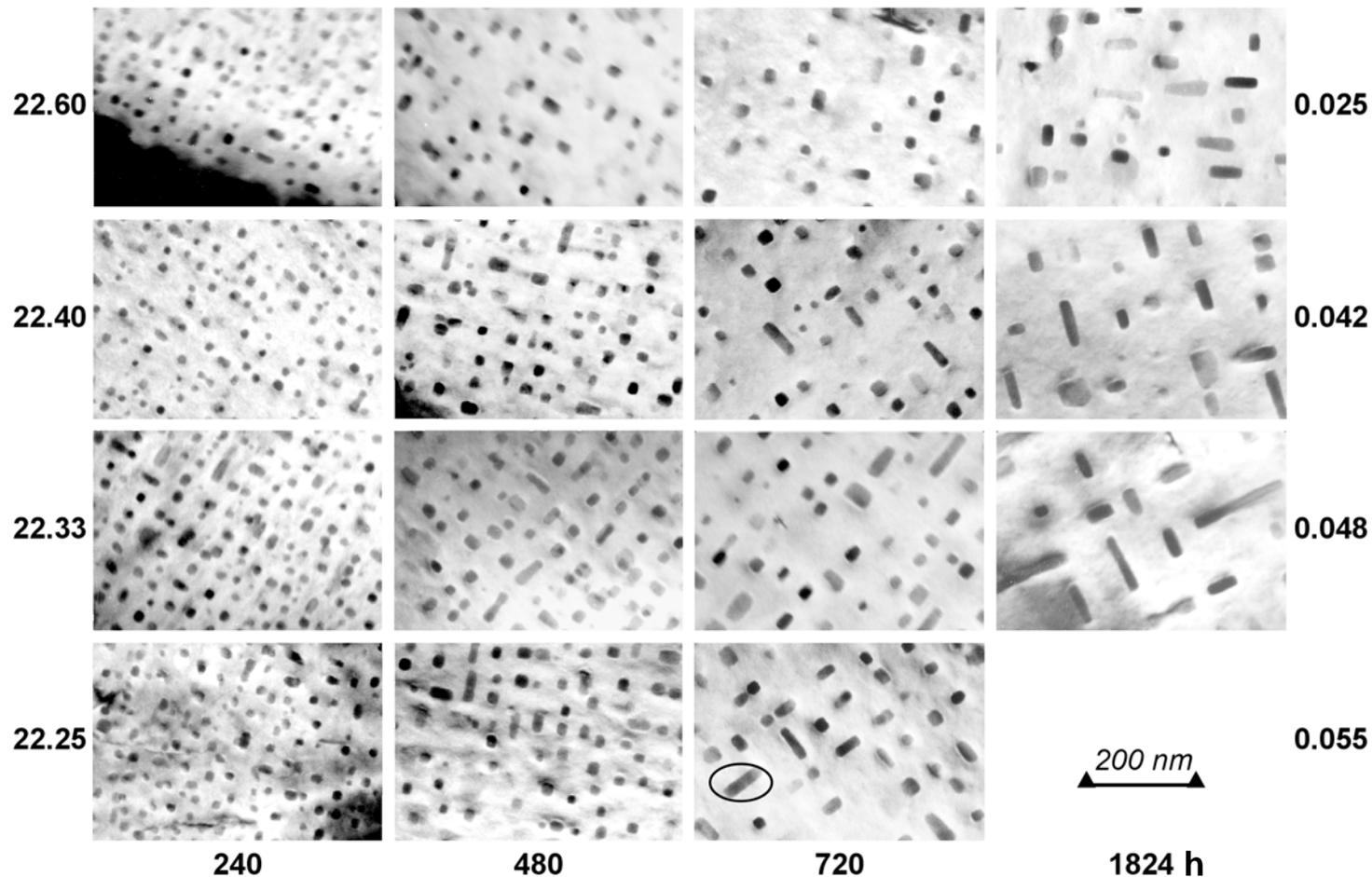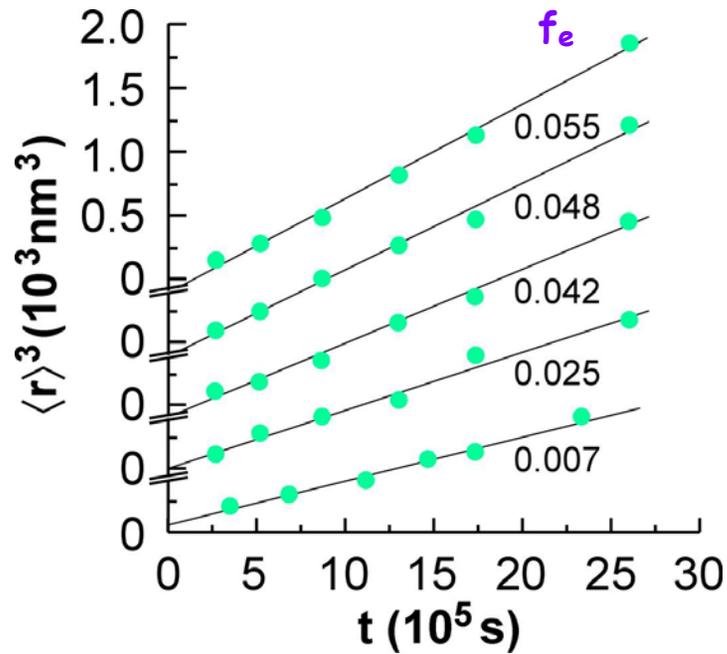
Data on the kinetics of coarsening at 650 °C, the only temperature at which all 5 alloys could be aged in the 2-phase $\gamma + \gamma'$ region. The slopes of the curves provide values of $k(f_e)$, which clearly increases with increasing f_e.
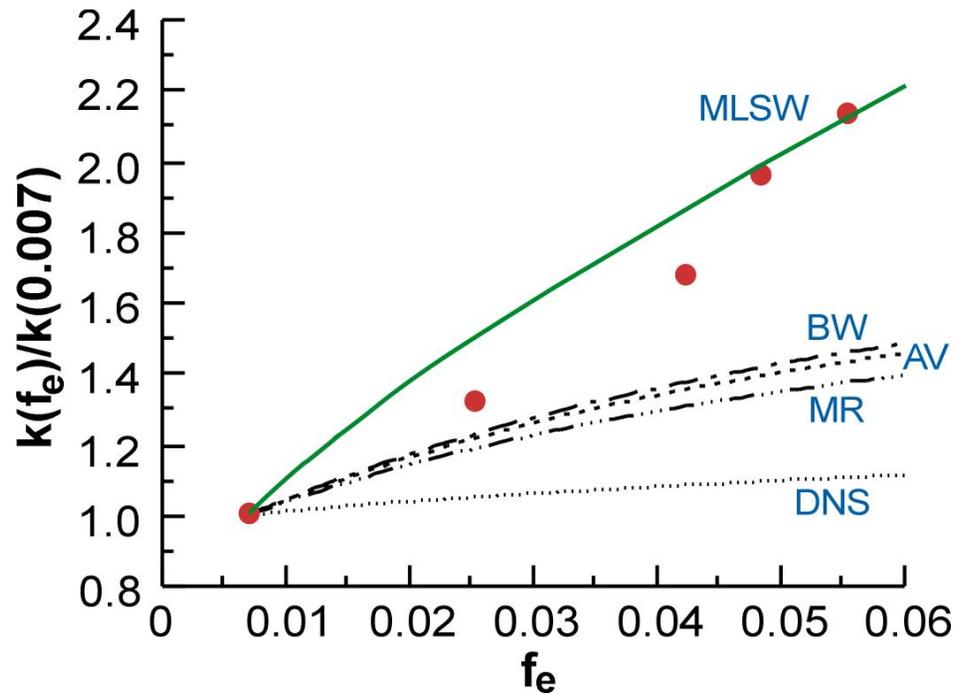
The ratio $k(f_e)/k(0.007)$ is compared with the predictions of several theories; the data shown are those for aging at 650 °C. This provides a completely unbiased comparison between theory and experiment. The dependence of $k(f_e)$ on f_e is very strong compared with predictions of all the theories shown earlier (the MLSW theory was omitted).

Coarsening of γ' in Ni-Al alloys at 800 °C
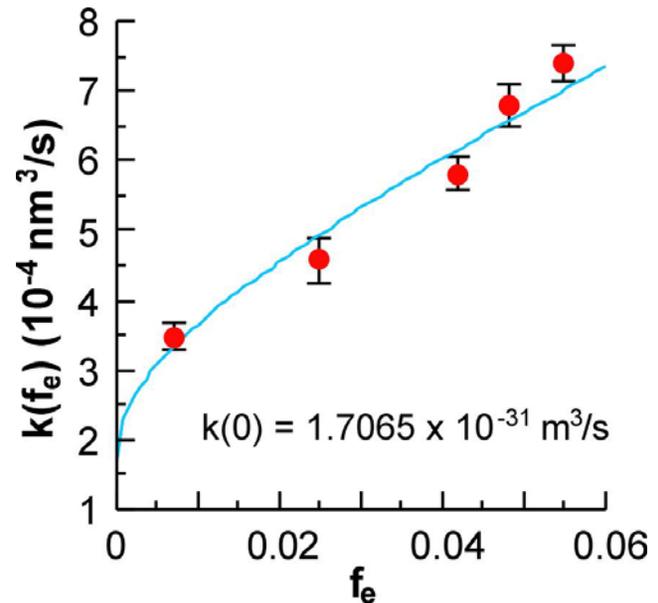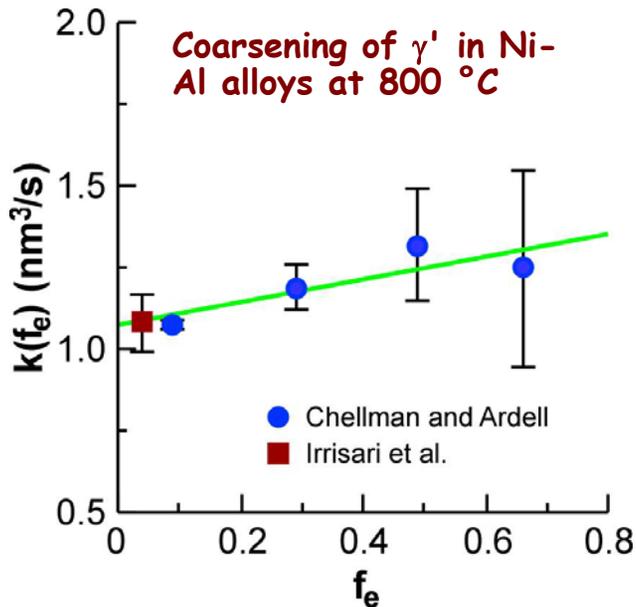
$k(0) = 1.7065 \times 10^{-31}$ m^3/s

The data on k(f_e) for the 5 inverse alloys aged at 650 °C were fit to the MLSW theory, yielding k(0) = 1.7065 ± 0.0917 × 10^{-31} m^{-3}/s. As can be seen, the agreement between the MLSW theory and experiment is quite good.

What is going on here?

- Why are the volume-fraction dependencies of coarsening kinetics in normal and inverse alloys so different (essentially zero in normal alloys and very strong in inverse alloys)? After all, the important physical parameters are identical in magnitude (interfacial free energy, lattice mismatch, elastic constant mismatch).

- However, diffusion is much slower in the ordered alloy matrix than it is in the solid solution.

- Recent atomistic calculations (Mishin, for example), and experimental results (Seidman's group) provide clear evidence that the γ/γ' interface is not sharp, but diffuse.

- Since the degree of long-range order must vary across the interface, and chemical diffusion in the ordered phase is much slower than it is in the disordered solid solution, what are the consequences?

- These observations provide the foundation for the new theory.

Part 3

The TIDC theory

Monte-Carlo calculation of the equilibrium composition profile of a flat (001) γ/γ' interface in Ni-Al
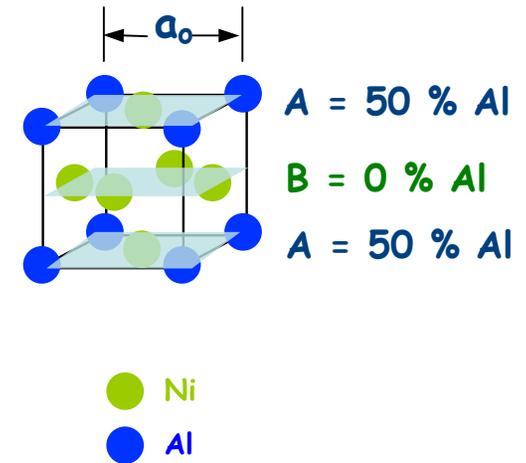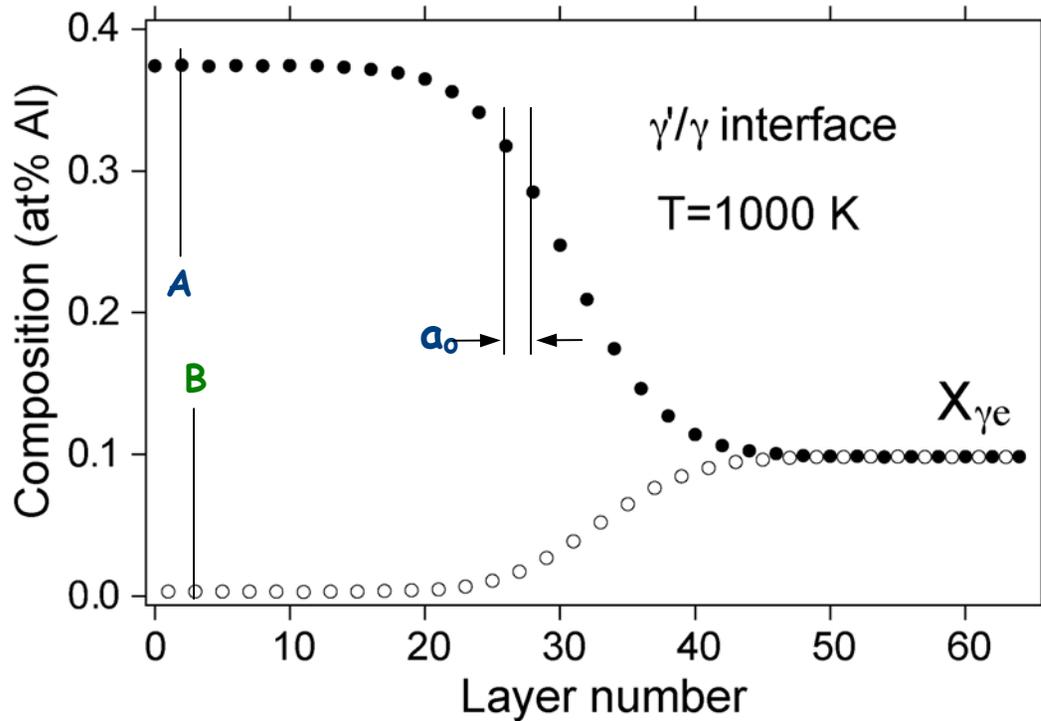
PRINCIPAL IDEA BEHIND THE TIDC THEORY

Since atoms must be transported through the non-sharp interface by diffusion in order that the precipitate grow or shrink, and diffusion is much slower in the ordered phase than in the disordered phase, the diffuse interface becomes a diffusion BOTTLENECK, especially as atoms approach the γ' phase.

We can also see immediately that no such diffusion bottleneck exists for coarsening in the inverse alloy, since now chemical diffusion in the ordered matrix is slower than in the interface.

Non-equilibrium composition profile around a growing γ' precipitate of radius $r > r^*$. The dashed curve shows the composition profile for a precipitate of radius r in equilibrium with a matrix of composition X_r. The width of the interface is δ, and the composition of the matrix phase is X_γ. The dotted horizontal line shows the thermodynamic equilibrium composition $X_{\gamma e}$.
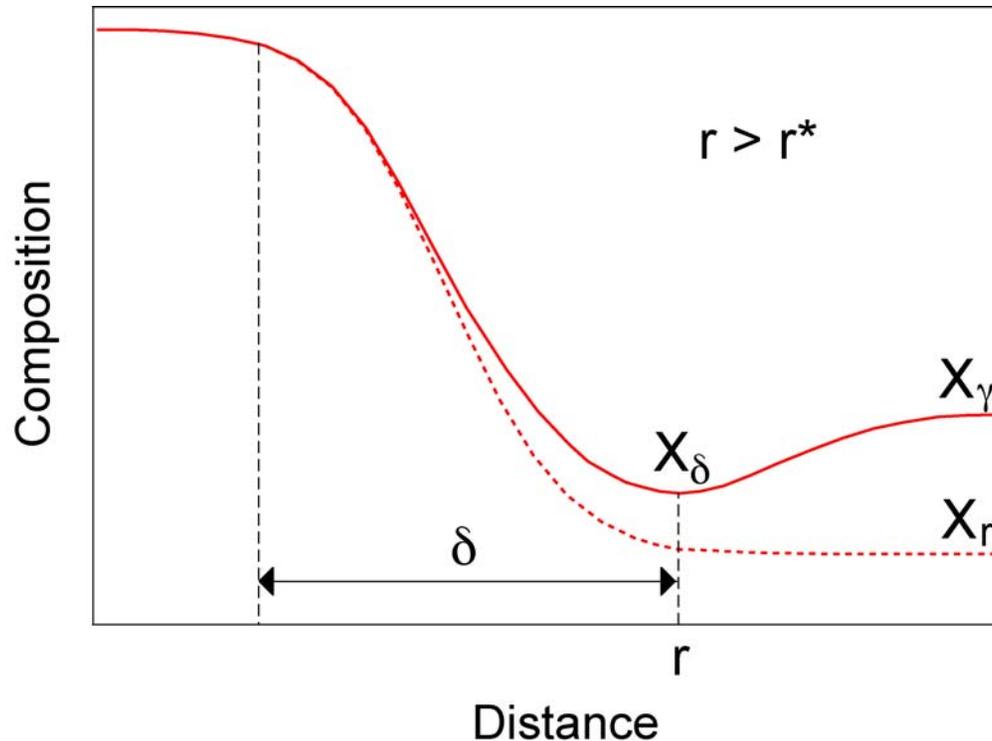
The flux of solute in the matrix (γ) phase, J_γ at r is given by the usual solution to the steady-state diffusion problem

$$J_\gamma = -D_\gamma \frac{X_\infty - X_r}{r}$$

The flux of solute through the interface, J_I, is estimated to be

$$J_I = -D_I \frac{X_\delta - X_r}{\lambda}$$

Because the flux is driven by the difference between chemical potentials of solute under conditions of local equilibrium at the interface ($X = X_r$) and the actual solute concentration, X_δ.

At steady-state $J_\gamma = J_I$, leading to the equation

$$X = \frac{r\overset{\circ}{D}_I X_r + \overset{\circ}{D} X}{r\overset{\circ}{D}_I + \overset{\circ}{D}}$$

Condition I: $r\overset{\circ}{D}_I$? $\overset{\circ}{D}$ ... $X_\delta \rightarrow X_r$ ... **normal coarsening**

Condition II: $\overset{\circ}{D}$? $r\overset{\circ}{D}_I$ ... $X_\delta \rightarrow X_\gamma$ ... **TIDC coarsening**

The growth rate of an individual precipitate under TIDC conditions is

$$\frac{dr}{dt} = \frac{\tilde{D}_I^{\%} l_c}{X_e} \; \frac{1}{r^*} - \frac{1}{r}$$

and the critical radius, r*, is given by

$$X = X_e + \frac{l_c}{r^*}$$

The growth rate of the average precipitate is given by

$$r^2 - r_o^2 = k_I t$$

where the rate constant, k_I, is now

$$k_I = \frac{32 \, \tilde{D}_I l_c}{81 \, X_e}$$

The kinetics of solute depletion is governed by the equation

$$X - X_e - \kappa_I t^{-1/2}$$

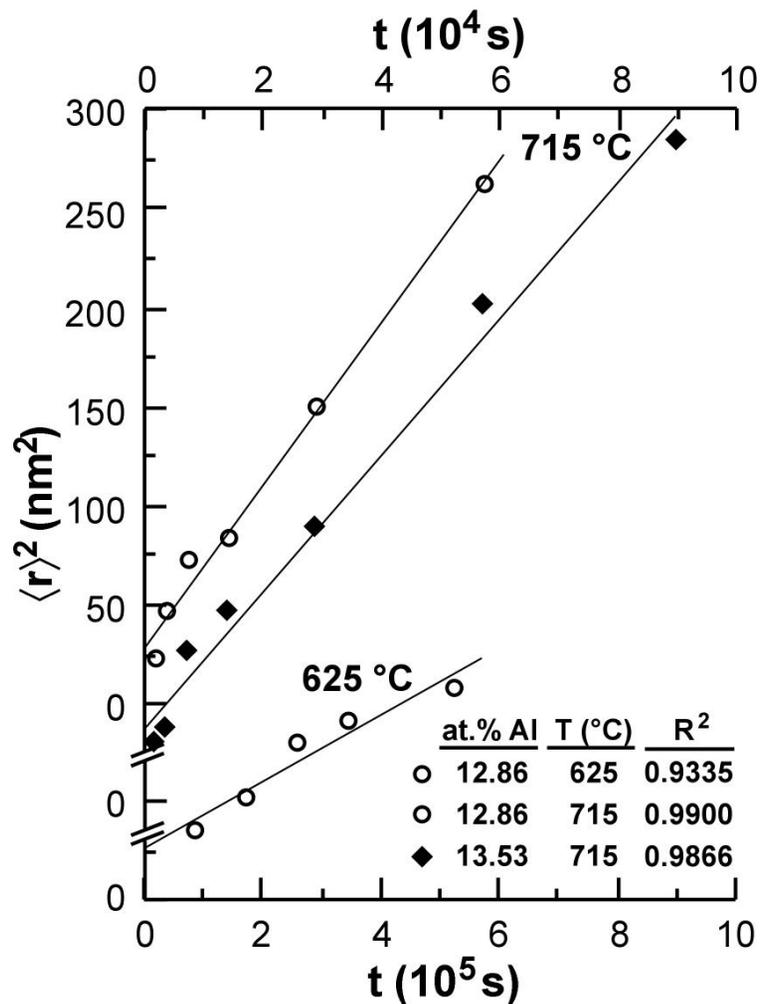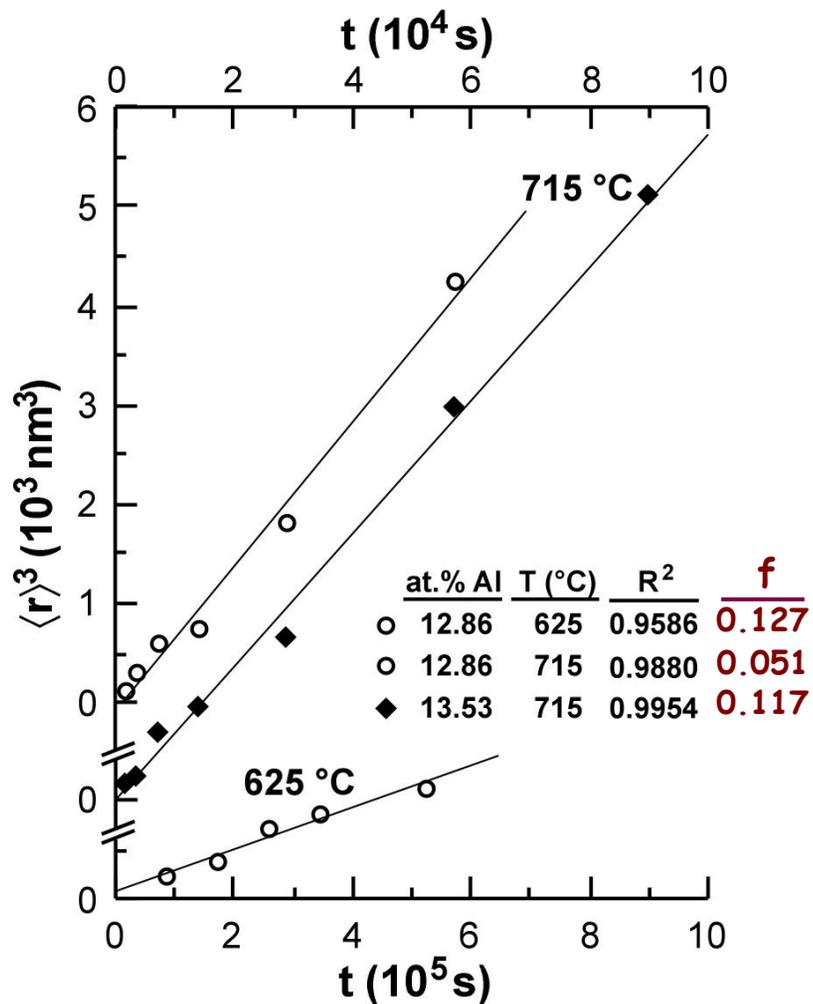**where the rate constant, κ_I, is now**

$$\kappa_I = \frac{\tilde{D}_I}{2 \, X_e \, l_c}$$

Kinetic exponents

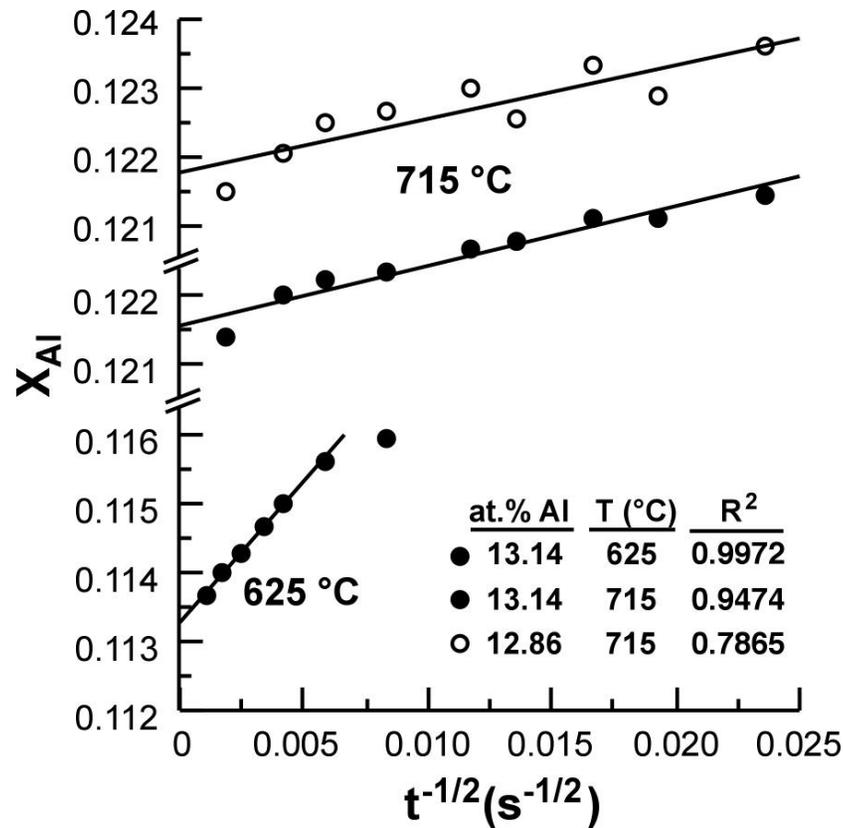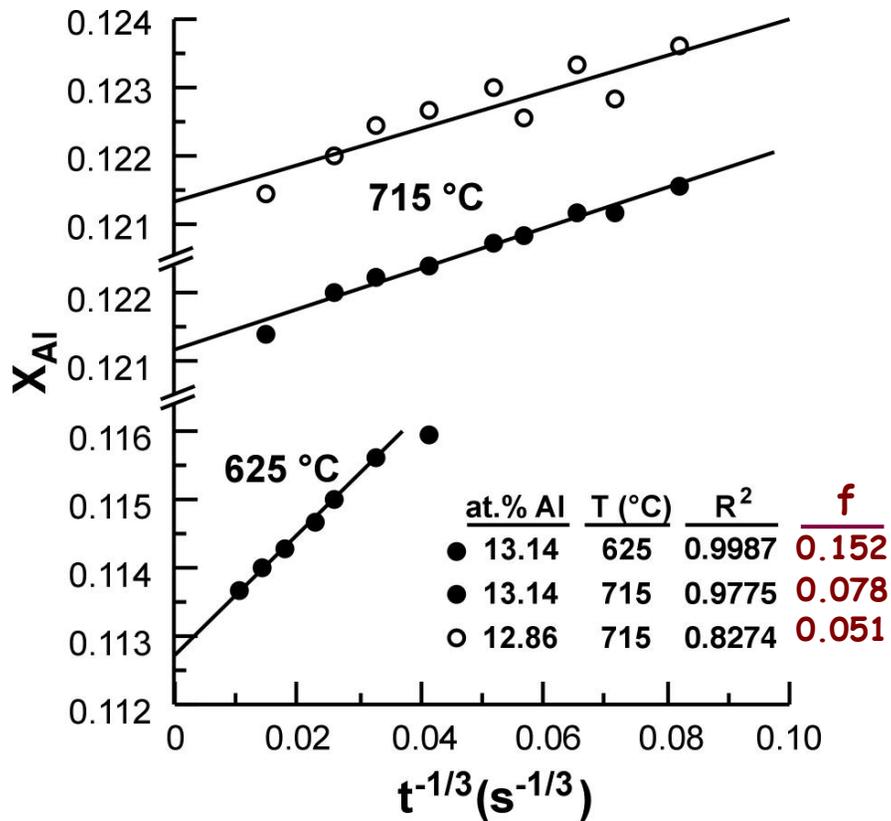|	TIDC	LSW
Growth of average particle	2	3
Solute depletion	-1/2	-1/3

The particle size distribution is given by the equation

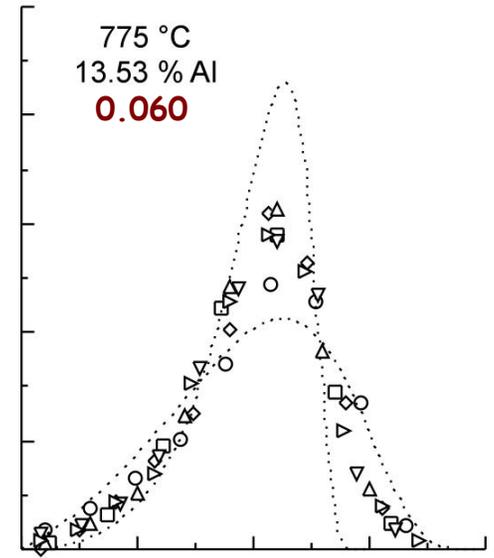$$h(z) = \frac{24\,z}{(2-z)^5}\,\exp\left(\frac{-3z}{2-z}\right) \quad ; \quad z \leq 2$$

But since $\langle z \rangle = 8/9$, and we need to compare experimental results expressed in terms of the variable $u = r/\langle r \rangle$, the appropriate distribution function is

$$g(u) = 8h(z)/9$$

with

$$u = 9z/8$$
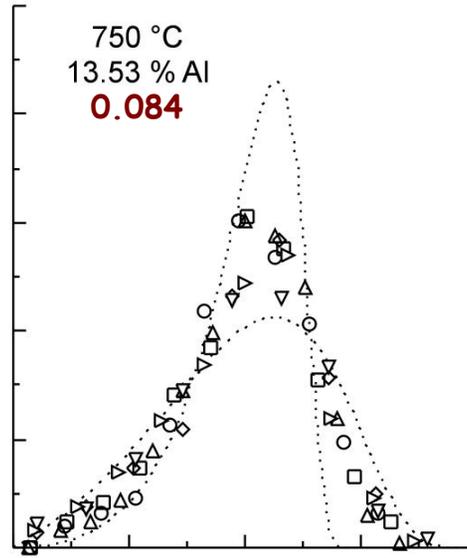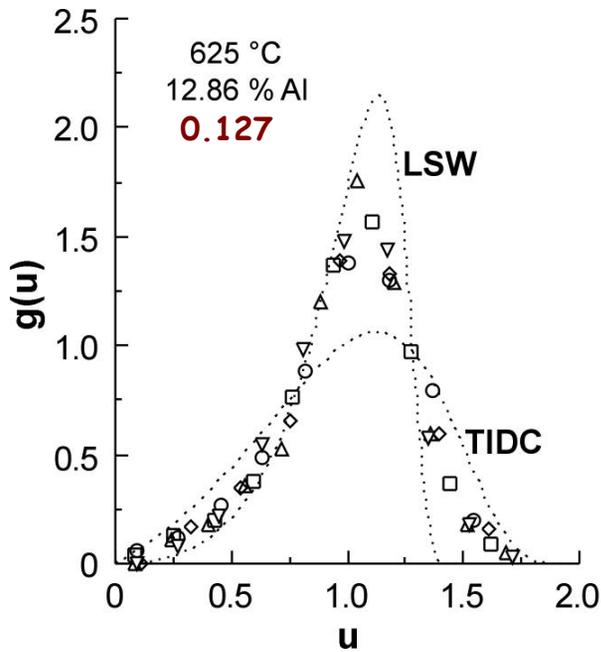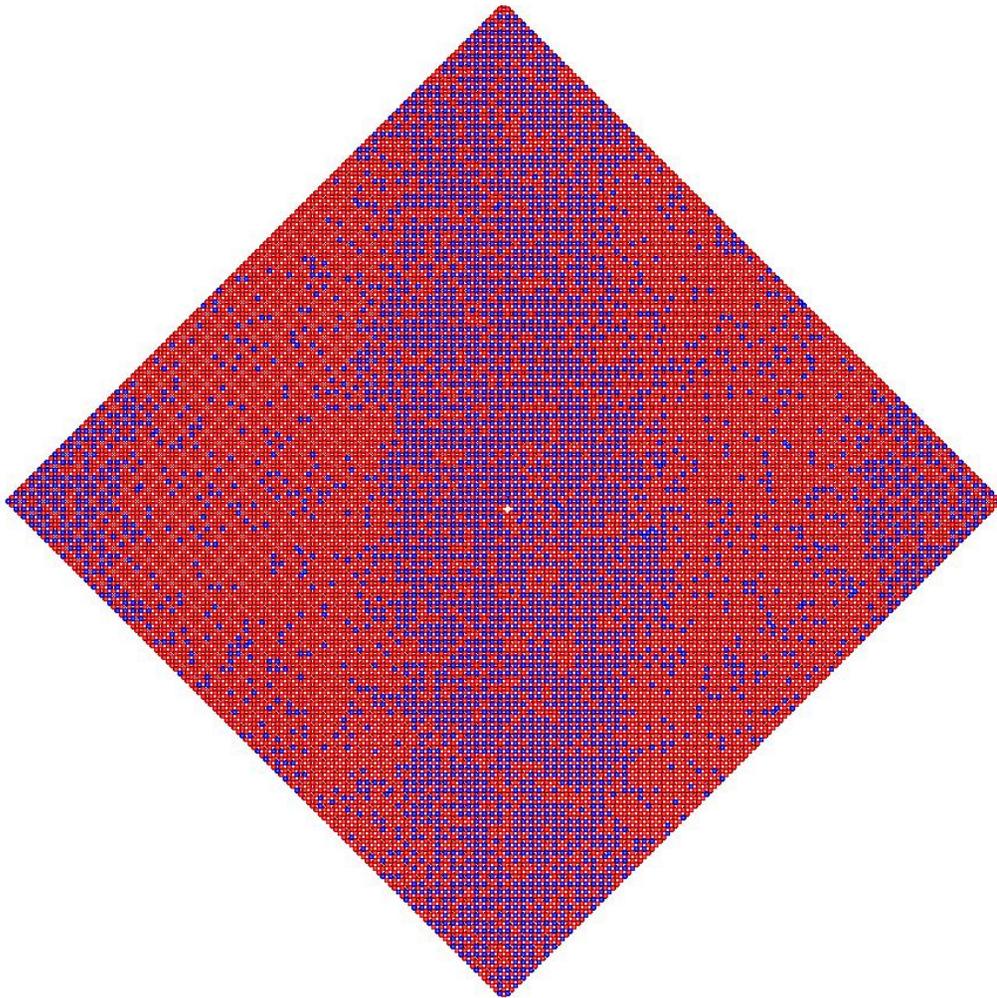
Atomistic calculations show that the γ/γ' interface is quite ragged in structure. This raggedness, we believe, might be dependent on size and perhaps justifies a relationship of the type $\delta \propto r^m$

If δ depends on r as r^m, it is easy to show that kinetic behavior of the kind

$$r^n - r_o^{\ n} = k_{nI}t$$

will be obeyed, where n = m + 2 and k_{nI} is another constant.

The kinetic data on γ' coarsening in Ni-Al alloys will certainly obey this equation, since they do quite well already for the extreme cases n = 2 and n = 3.

The main effect of this assumption is that the γ' PSDs will now also fit the TIDC theory quite well, as shown below, where the data on all aging times and alloy concentrations are combined:
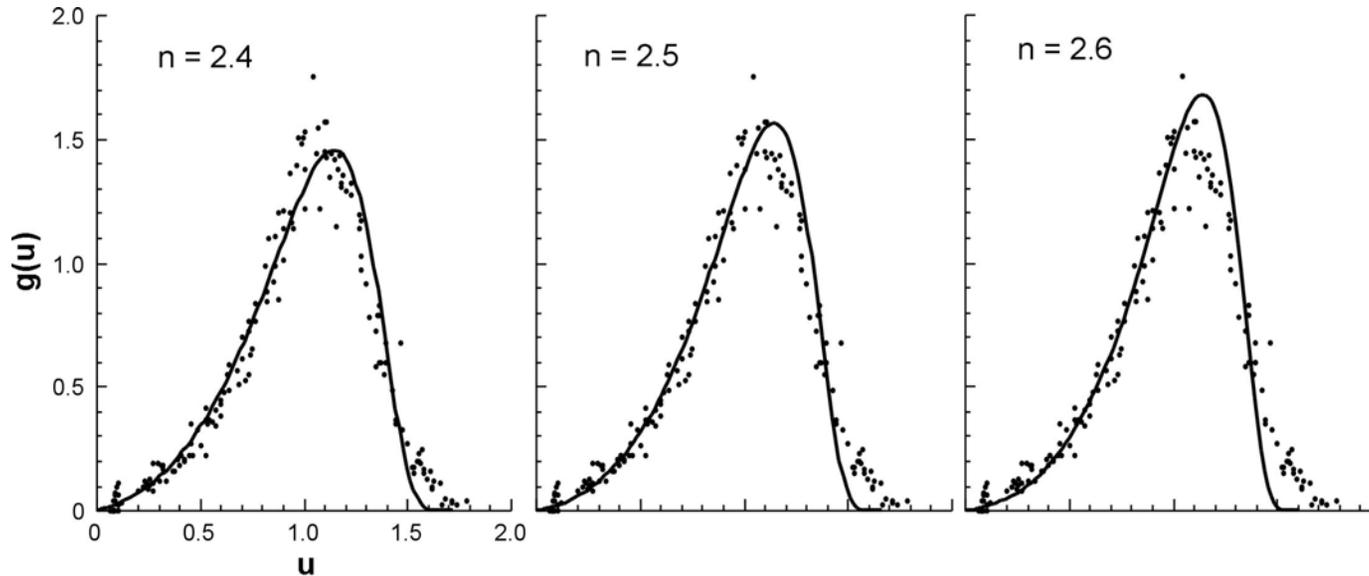
The fits to the data on n = 2.4 and n = 2.5 are quite exceptional !!!

SUMMARY

The TIDC theory agrees very well with the data on the kinetics of coarsening of Ni_3Al precipitates in normal Ni-Al alloys and is consistent with the complete absence of an effect of volume fraction on the rate constants for the kinetics of growth and solute depletion;

The experimentally measured PSDs agree about equally well with those predicted by the LSW and TIDC theories, but the fit is best when the TIDC theory allows for a size-dependent interface width of the type $\delta \propto r^m$, leading to the kinetic laws of the type $\langle r \rangle^n \propto t$ and $X_\gamma - X_{\gamma e} \propto t^{-1/n}$, where $n = m + 2 \approx 2.4$;

No attempt was made to manipulate the kinetic data to favor the TIDC theory (e.g. eliminating data at longer aging times and larger particle sizes where the condition $D^0 \gtrless r D^0_I$ is possibly no longer valid).

SUMMARY (continued)

The interfacial free energies and diffusion coefficients obtained from analysis of the data on coarsening (m = 0 or equivalently n = 2) are generally in good agreement with other measurements, especially keeping in mind possible uncertainties in σ (4 < σ < 18 mJ/m^2);

The LSW theory should be valid in systems in the diffuse interface is not a diffusion bottleneck. Examples are Co precipitates in Cu, Al$_3$Li precipitates in Al (very narrow interface) and solid precipitates in a liquid matrix (fast attachment kinetics). Consequently, strong effects of volume fraction on kinetics is observed in these systems. And let's not forget the results on coarsening in the inverse alloy!!!

A paper on the TIDC theory was recently accepted for publication in Nature Materials