# CINÉTIQUE DE CROISSANCE INSTATIONNAIRE POUR SYSTÈME MULTICOMPOSÉ AVEC DIFFUSION CROISÉE

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# SOLUTION ANALYTIQUE ET COUPLAGE CALPHAD

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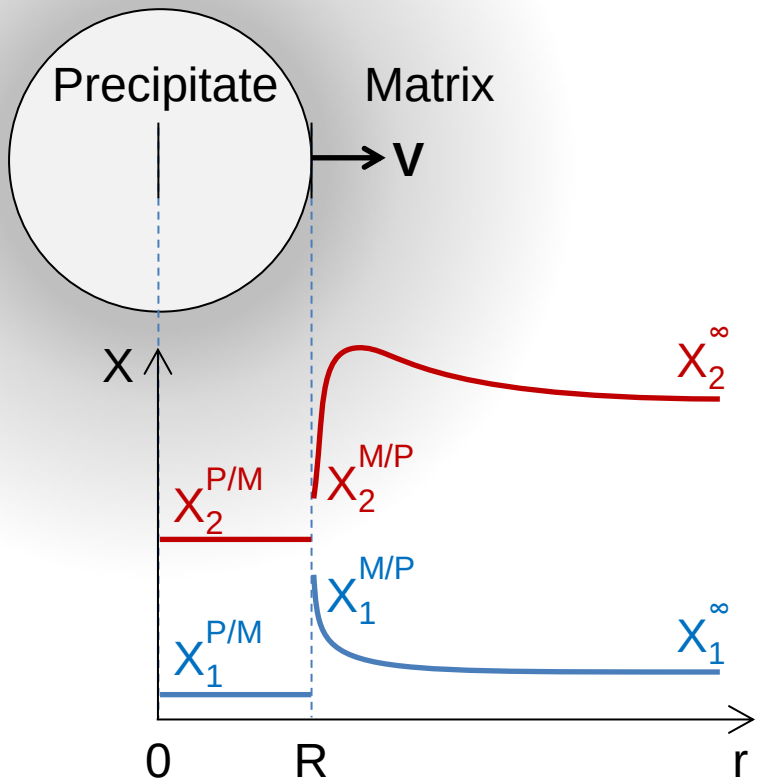
Campus de La Doua, Université Claude Bernard – Lyon 1

# GROWTH OF A SPHERICAL PARTICLE IN A MULTICOMPONENT ALLOY

## MATHEMATICAL PROBLEM: ISOTHERMAL GROWTH IN A SEMI-INFINITE MATRIX PHASE

- Semi-infinite matrix phase M
- Spherical precipitate P, no curvature
- Isothermal system T
- N solute species
- Constant diffusion in M
- Homogeneous precipitate $\langle X_i^P \rangle^P = X_i^{P/M}$
- Constant and equal densities




- Solute mass conservation in the matrix

$$\frac{\partial X_i^M}{\partial t} = \sum_{j=1}^{N} \frac{D_{ij}^M}{r^2} \frac{\partial}{\partial r}\left( r^2 \frac{\partial X_j^M}{\partial r} \right)$$

- Interfacial solute balance at r=R

$$V\left(X_i^{M/P} - X_i^{P/M}\right) = -\sum_{j=1}^{N} D_{ij}^M \left.\frac{\partial X_j^M}{\partial r}\right|_{P/M} + \frac{R}{3}\frac{\partial X_i^{P/M}}{\partial t}$$

- Thermodynamic equilibrium at interface

$$T = F^{M/P}\left[\{X_i^{M/P}\}_{1\le i\le N}\right]$$

$$X_i^{P/M} = \Phi_i^{P/M}\left[\{X_i^{M/P}\}_{1\le i\le N}\right]$$

- Condition at infinity when $r \to \infty$

$$\lim_{r\to\infty} X_i^M(r,t) = X_i^\infty$$

- Initial conditions (t = 0 s)

$$\forall r > R_0,\ X_i^M = X_{i,0}, \qquad T = T_0, \quad R = R_0$$

# GROWTH OF A SPHERICAL PARTICLE IN A MULTICOMPONENT ALLOY

## ANALYTICAL SOLUTION *[GUILLEMOT GANDIN, Acta Mater. 97 (2015) 419]*

- The solute profile is a N-linear combination of the solution for the 1-component expression *[ZENER, J. of Appl. Phys. 20 (1949) 950] [AARON et al., J. of Appl. Phys. 41 (1970) 4404] [HUNZIKER, Acta Mater. 49 (2001) 4191]*

$$X_i^M(r,t) = X_i^\infty + \sum_{j=1}^{N} K_j\, U_{ij}\, F\left(\frac{r^2}{B_j\, t}\right) \qquad \text{where} \quad F(u) = e^{-u/4}/\sqrt{u} - \left(\sqrt{\pi}/2\right) \operatorname{erfc}\left(\sqrt{u}/2\right)$$

with $B_j$ is the j-eigenvalue of matrix $\mathbf{D}^M$

$K_j$ is the norm of the eigenvector $\mathbf{K}_j$ of matrix $\mathbf{D}^M$, with i-component $K_{ij} = K_j\, U_{ij}$

$U_{ij}$ is the i-component of the j-unitary eigenvector $\mathbf{U}_j$ of matrix $\mathbf{D}^M$

- A unique solution for the interface position is given by $R^2 = \lambda' t$ .
  $\lambda'$ is determined by the N-interfacial solute balances:

$$\left(\mathbf{X}^{M/P} - \mathbf{X}^{P/M}\right) = \Lambda(\lambda') \left(\mathbf{X}^{M/P} - \mathbf{X}^{\infty}\right) \text{ where } \quad \Lambda(\lambda')_{ij} = \sum_{k=1}^{N} U_{ik}\, U_{kj}^{-1}\, G\left(\frac{\lambda'}{B_k}\right) \quad \text{and} \quad G(u) = -4\,\frac{F'(u)}{F(u)}$$

- The composition profile is computed when knowing the norm of the eigenvectors. $K_j$ are determined by solving the system:

$$\mathbf{K} = \Gamma(\lambda') \left(\mathbf{X}^{M/P} - \mathbf{X}^{\infty}\right) \qquad \text{where} \qquad \Gamma(\lambda')_{ij} = U_{ij}^{-1} / F\left(\lambda'/B_i\right)$$

# APPLICATION

## SINGLE γ' PRECIPITATE IN A γ MATRIX - NI-AL-CR ALLOY

### ❑ Physical parameters

| | | | | |
|---|---|---|---|---|
| ▪ Thermodynamics | database | NI20 | | Thermo-Calc |
| ▪ Alloy composition | $X_{Al,0}$ | 7.56 | at% | used as $X^{\infty}_{Al}$ |
| | $X_{Cr,0}$ | 8.56 | at% | used as $X^{\infty}_{Cr}$ |
| ▪ Fixed temperature | $T_0$ | 600 | °C | |
| ▪ Initial radius | $R_0$ | 0 / 0.8 | nm | "semi-infinite"/finite domain |
| ▪ Droplet radius | $R_f$ | -- / 10.6 | nm | "semi-infinite"/finite domain |
| ▪ Interfacial energy | $\sigma^{\gamma/\gamma'}$ | $27 \cdot 10^{-3}$ | J m$^{-2}$ | *[BOOTH-MORRISON et al.,* |
| ▪ Molar volume | $V_m$ | $6.8 \cdot 10^{-6}$ | m$^3$ mol$^{-1}$ | *Acta Mater. 56 (2008) 3422]* |

### ❑ Numerical model

| | | | | | | |
|---|---|---|---|---|---|---|
| ▪ FCC_L12#2 (γ') | $\mathbf{D}^{\gamma'}$ | Al / Cr | Al: 1, 0 / Cr: 0, 1 | $10^{-19}$ m$^2$ s$^{-1}$ | | taken artificially large |
| ▪ Initial radius | $R_0$ | | 0 / 0.8 | nm | | "semi-infinite"/finite domain |
| ▪ Droplet radius | $R_f$ | | 100 / 10.6 | nm | | "semi-infinite"/finite domain |
| ▪ Mesh | $n^{\gamma}$, $n^{\gamma'}$ | | 500 | - | | |
| ▪ Time step | $\Delta t$ | | $5 \cdot 10^{-2}$ | s | | |

# APPLICATION

## SINGLE γ' PRECIPITATE IN A γ MATRIX - NI-AL-CR ALLOY

- FCC_L12#1 (γ) $D^{\gamma}_{cro}$

| | Al | Cr |
|---|---|---|
| Al | 20.8 | 8.59 |
| Cr | 8.13 | 3.82 |

$10^{-21}$ m$^2$ s$^{-1}$

*[LANGER et al., Acta Mater. 60 (2012) 1871]*

$D^{\gamma}_{inf}$

| | Al | Cr |
|---|---|---|
| Al | 20.8 | **0** |
| Cr | 8.13 | 3.82 |

$10^{-21}$ m$^2$ s$^{-1}$

$D^{\gamma}_{sup}$

| | Al | Cr |
|---|---|---|
| Al | 20.8 | 8.59 |
| Cr | **0** | 3.82 |

$10^{-21}$ m$^2$ s$^{-1}$

$D^{\gamma}_{dia}$

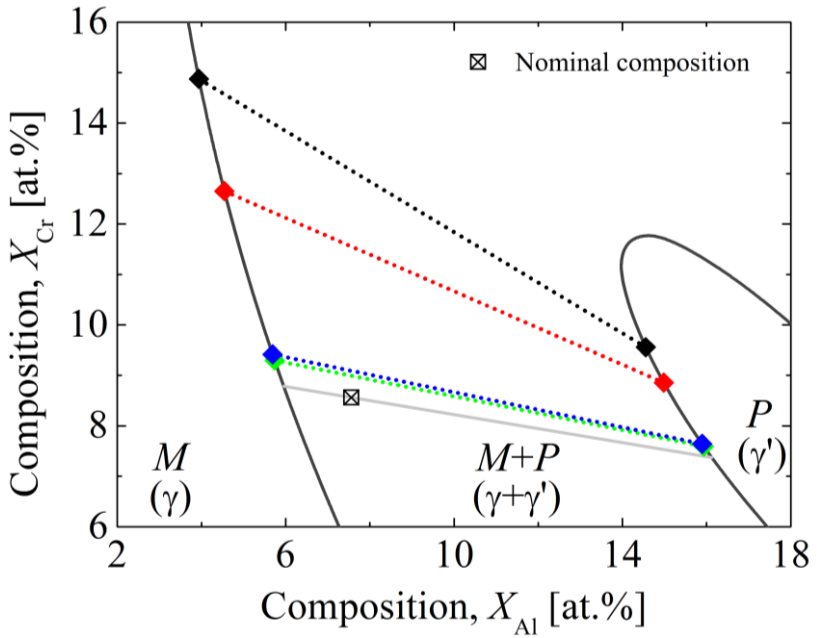
| | Al | Cr |
|---|---|---|
| Al | 20.8 | **0** |
| Cr | **0** | 3.82 |

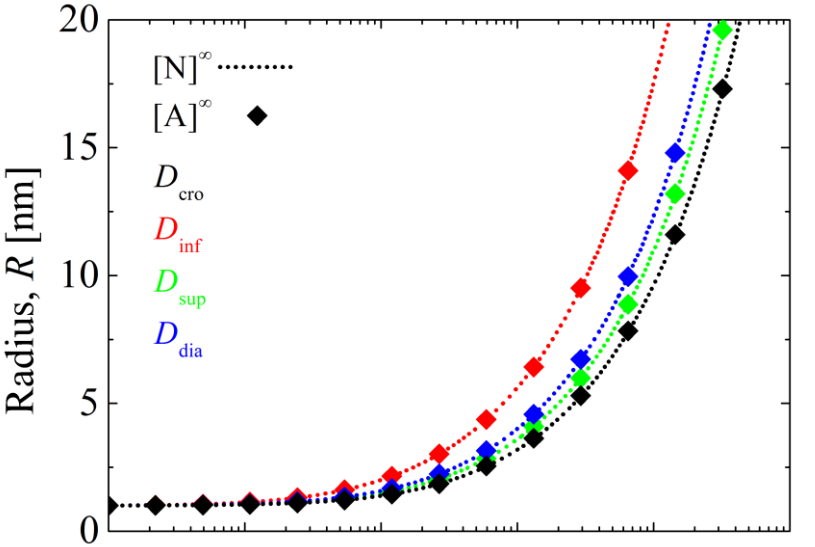
$10^{-21}$ m$^2$ s$^{-1}$

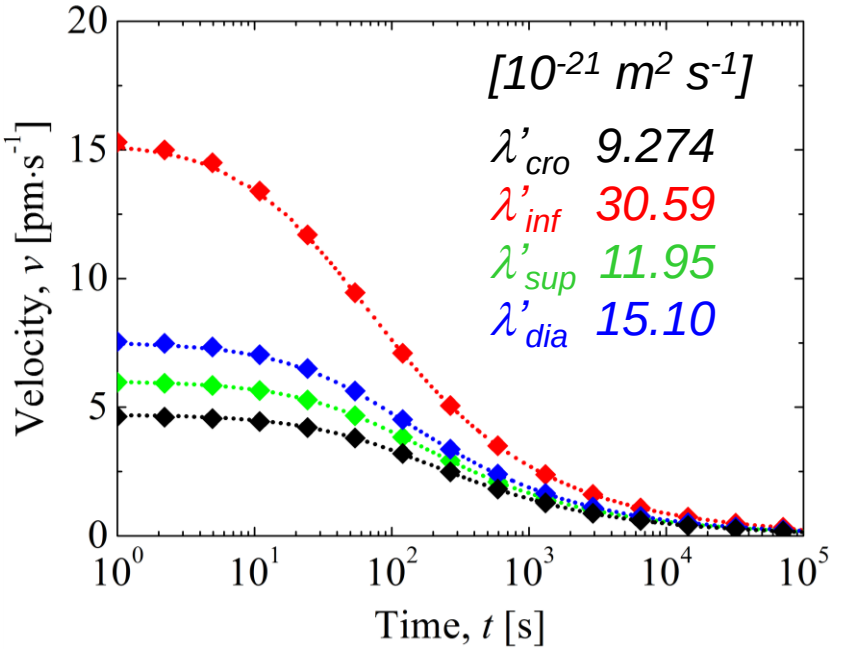
# RESULTS

## SINGLE γ' PRECIPITATE IN A γ MATRIX - NI-AL-CR ALLOY

- Analytical solutions ([A] diamonds symbols) superimpose on the numerical solution ([N] dotted curves) for all matrices
- Strong effect of the γ diffusion matrix on the growth velocity of the γ' precipitate
- The selected tie-line depends on $\mathbf{D}^{\gamma}$
- Computation time: [N] 1 h vs. [A] few s



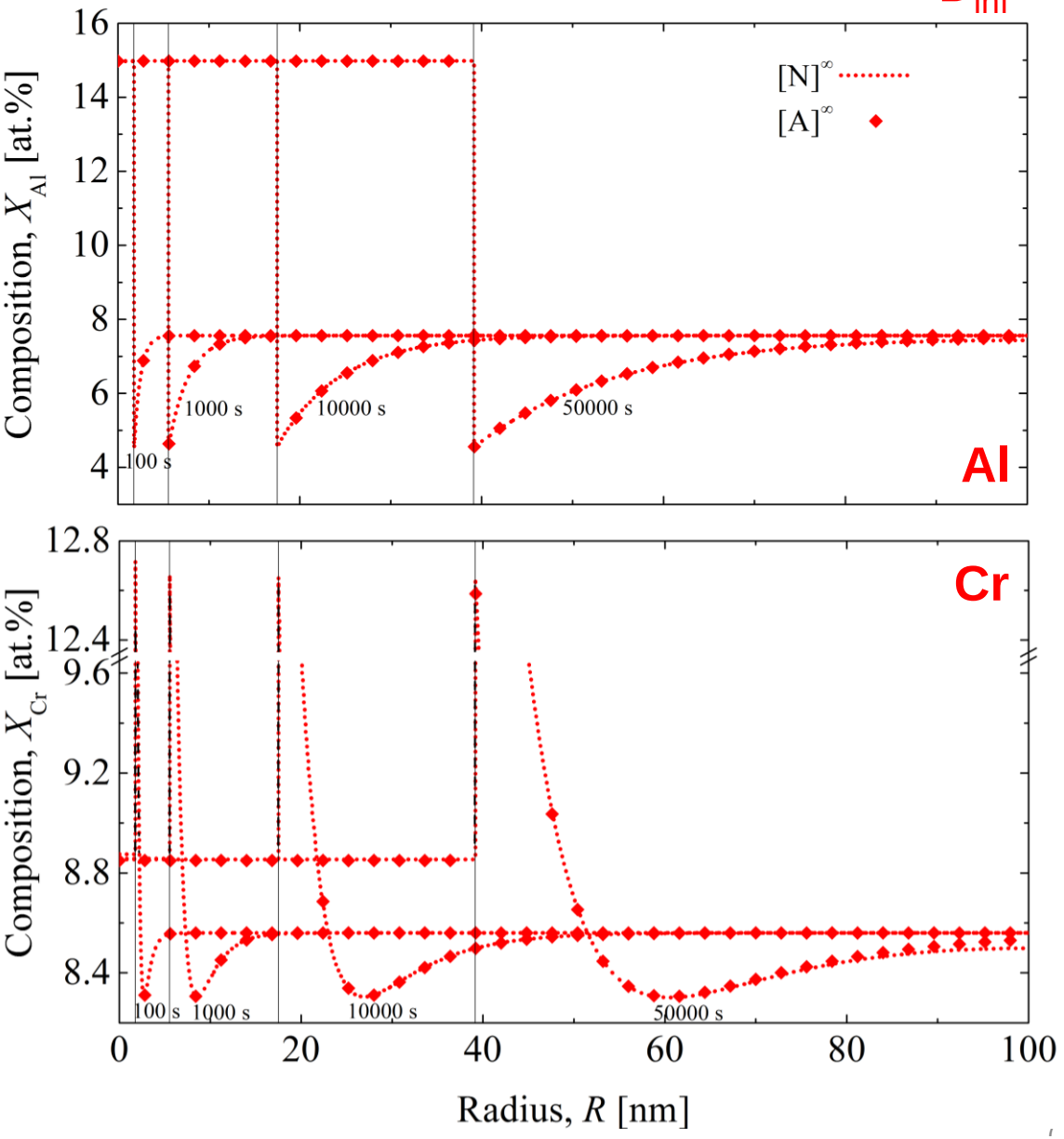
# RESULTS

## SINGLE γ' PRECIPITATE IN A γ MATRIX - NI-AL-CR ALLOY

- The analytical solution ([A] diamonds symbols) super-imposes on the numerical solution ([N] dotted curves)
- Al depletes / Cr accumulates ahead of the interface
- A typical non monotonous composition profile is found for Cr (cross diffusion effect)

➔ Validation of the N-component analytical solution for the growth of a single precipitate with approximations:

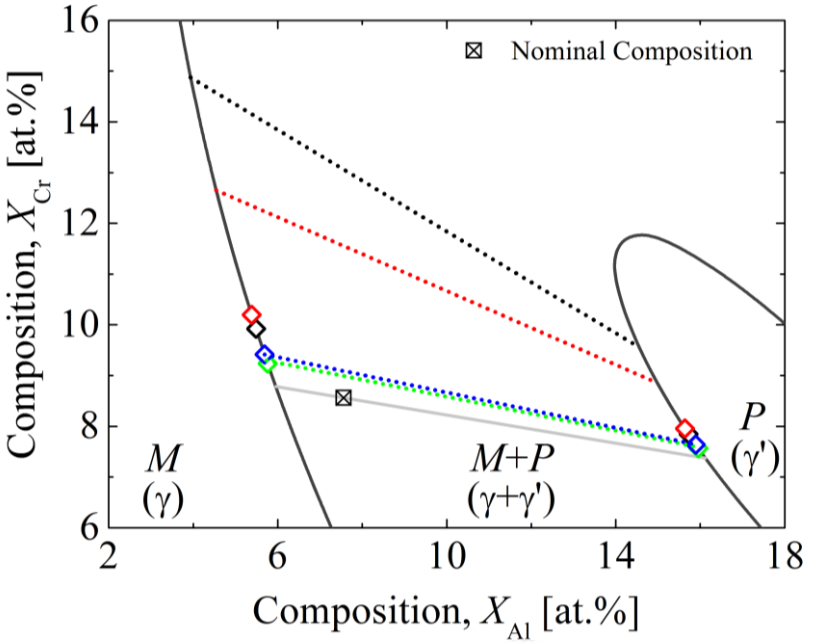
- *isothermal system*
- *semi-infinite matrix*
- *no curvature effect*

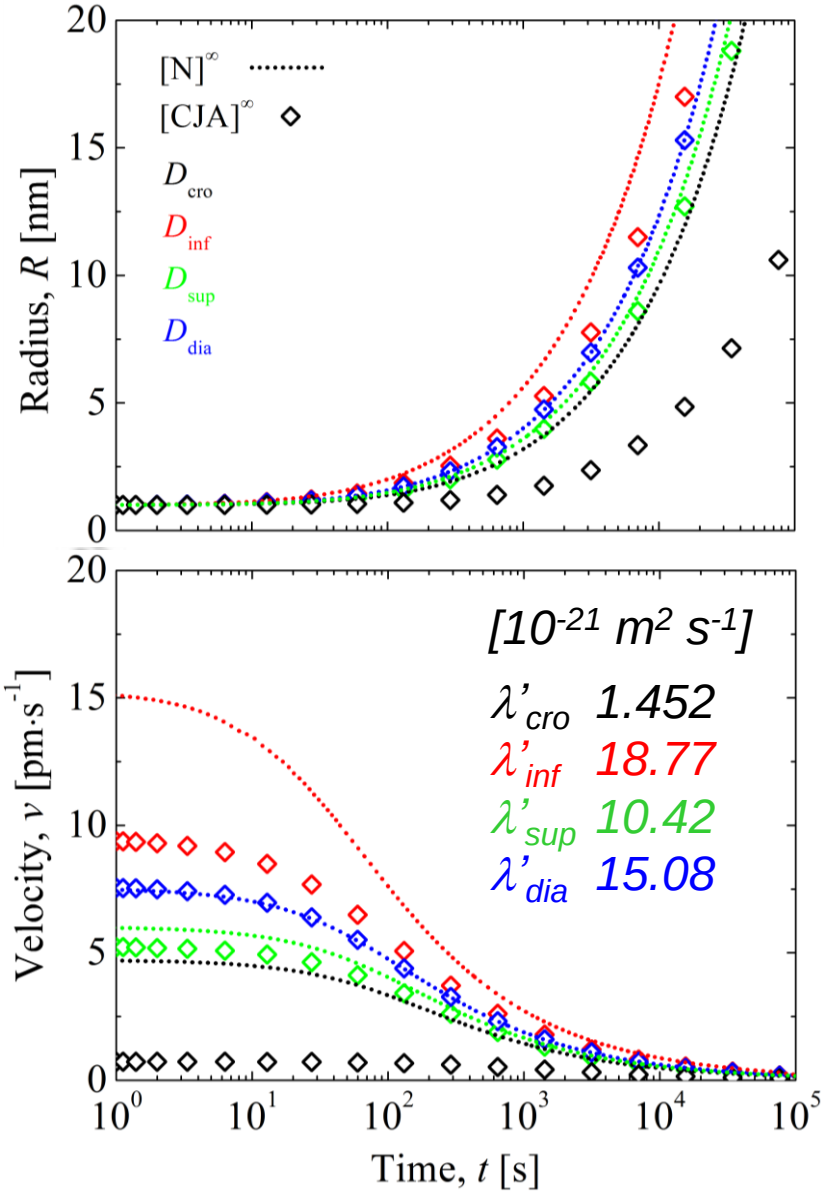


# COMPARISON WITH LITERATURE *[CHEN et al. model, Acta Mater. 56 (2008) 1890]*

## SINGLE γ' PRECIPITATE IN A γ MATRIX - NI-AL-CR ALLOY

- The CHEN et al. solution ([CJA] open diamonds symbols)
  - does not verify the exact solution,
  - is only an approximation that substantially deviates from the exact solution (e.g., $D_{cro}$),
  - is only valid with no interaction between species (i.e., $D_{dia}$),
  - provides different λ' growth parameters.

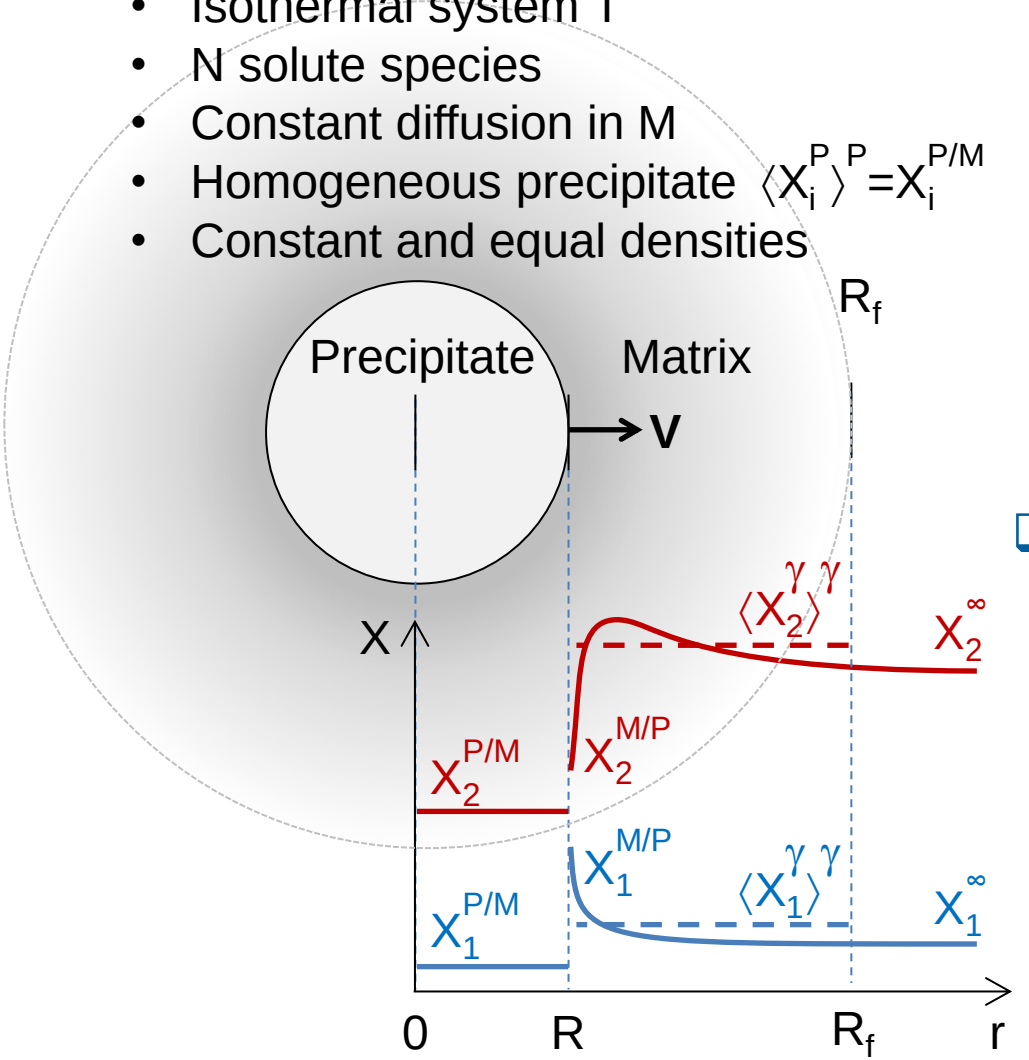


# EXTENSIONS

## GROWTH IN A FINITE DOMAIN AND EFFECT OF CURVATURE

- *Finite matrix phase M (limited by $R_f$)*
- *Spherical precipitate P with curvature*
- Isothermal system T
- N solute species
- Constant diffusion in M
- Homogeneous precipitate $\langle X_i^P \rangle^P = X_i^{P/M}$
- Constant and equal densities




### ❑ Global balances

- total mass $g^{\gamma'} + g^{\gamma} = 1$ with $g^{\gamma'} = \left(\frac{R}{R_f}\right)^3$
- solute mass $g^{\gamma'} \langle X_i^{\gamma'} \rangle^{\gamma'} + g^{\gamma} \langle X_i^{\gamma} \rangle^{\gamma} = X_{i,0}$

Providing the precipitate size R and its average composition are known, the average matrix composition can be computed

### ❑ Curvature

$$T = F^{M/P}\left[\{X_i^{M/P}\}_{1\le i\le N} ; \Delta G_\kappa\right]$$

$$X_i^{P/M} = \Phi_i^{P/M}\left[\{X_i^{M/P}\}_{1\le i\le N} ; \Delta G_\kappa\right]$$

$$\Delta G_\kappa = 2\,\sigma^{P/M}\,V_m^P / R$$

# EXTENSIONS

!?

CHOICE FOR MATRIX COMPOSITION AT ∞ IN $\left(\mathbf{x}^{\gamma/\gamma'} - \mathbf{x}^{\gamma'/\gamma}\right) = \Lambda(\lambda')\left(\mathbf{x}^{\gamma/\gamma'} - \tilde{\mathbf{x}}^{\infty}\right)$

$$X_i^{\gamma}(r,t) = \tilde{X}_i^{\infty}(t) + \sum_{j=1}^{N} K_j U_{ij} F\left(\frac{r^2}{B_j t}\right)$$

- Choice 1: use of the global mass balance

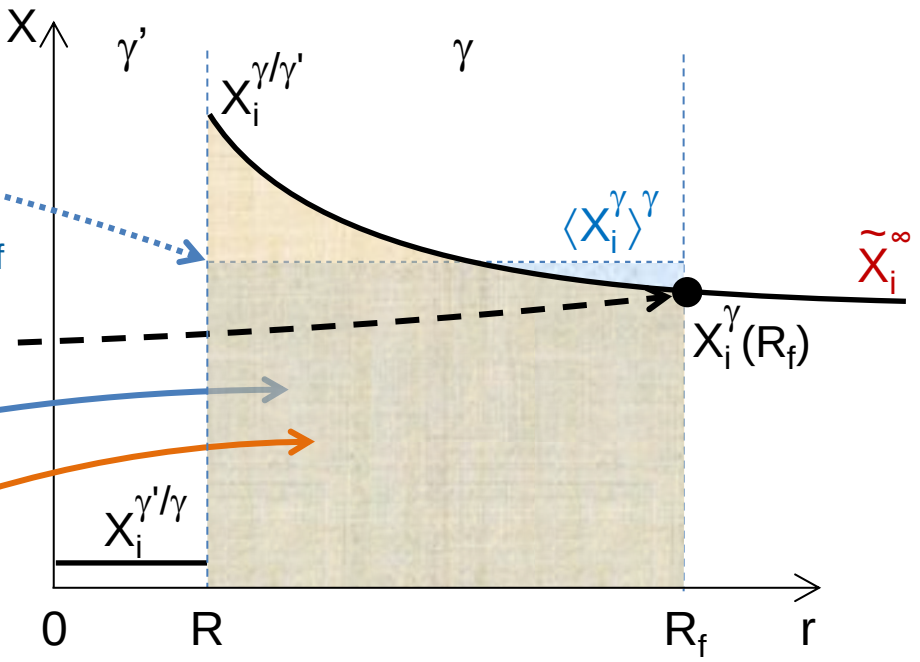
$$\tilde{X}_i^{\infty}(t) = \langle X_i^{\gamma} \rangle^{\gamma}$$

- Choice 2: use of the analytical profile at $R_f$

$$\tilde{X}_i^{\infty}(t) = X_i^{\gamma}(r=R_f, t)$$

- Choice 3: integral method

$$\frac{4}{3}\pi(R_f^3 - R^3)\,\langle X_i^{\gamma} \rangle^{\gamma} = \int_R^{R_f} X_i^{\gamma}(r,t)\, 4\pi r^2\, dr$$




➔ mathematical expression for $\tilde{X}_i^{\infty}(t)$ provided in

*[GUILLEMOT GANDIN, Acta Mater. 97 (2015) 419]*

# APPLICATION

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| ▪ **Interfacial energy** | $\sigma^{\gamma/\gamma'}$ | **$27 \cdot 10^{-3}$** | **J m$^{-2}$** | *[BOOTH-MORRISON et al., Acta Mater. 56 (2008) 3422]* |
| ▪ **Molar volume** | $V_m^{\gamma'}$ | **$6.8 \cdot 10^{-6}$** | **m$^3$ mol$^{-1}$** | |

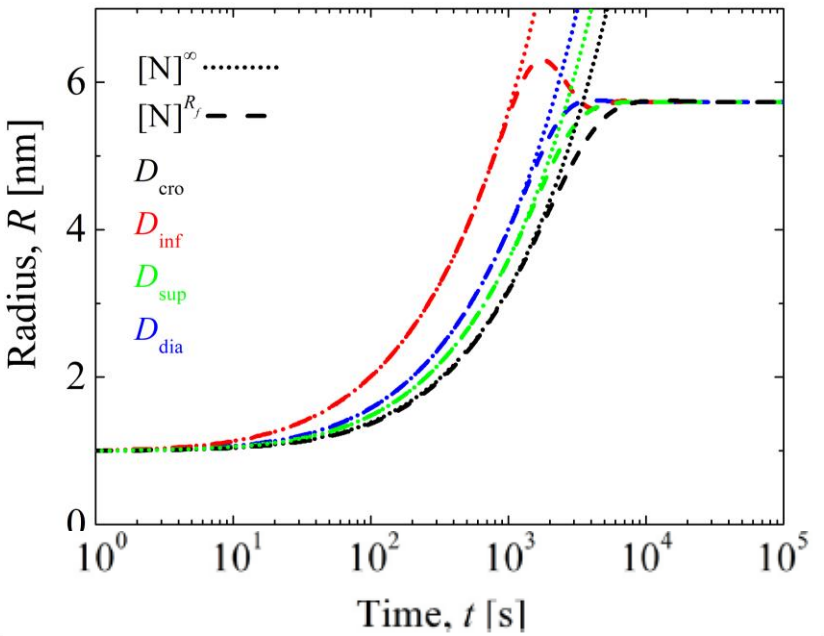
### ❑ Numerical model

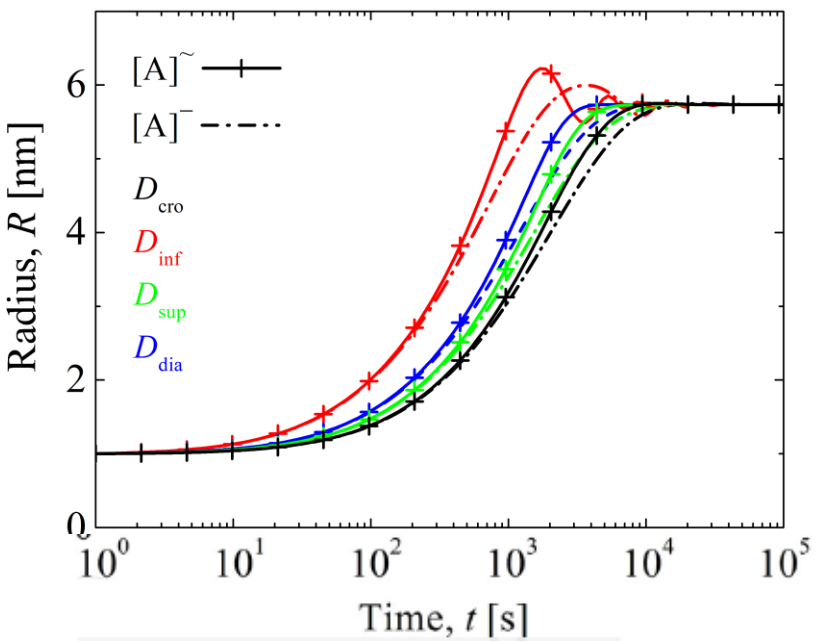
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ▪ FCC_L12#2 (γ') | $D^{\gamma'}$ | | Al | Cr | | | taken artificially large |
| | | Al | 1 | 0 | $10^{-19}$ m$^2$ s$^{-1}$ | | |
| | | Cr | 0 | 1 | | | |
| ▪ Initial radius | $R_0$ | | 00 / **0.8** | | nm | "infinite"/**finite** domain | |
| ▪ Droplet radius | $R_f$ | | 100 / **10.6** | | nm | "infinite"/**finite** domain | |
| ▪ Mesh | $n^{\gamma}$, $n^{\gamma'}$ | | 500 | | - | | |
| ▪ Time step | $\Delta t$ | | $5 \cdot 10^{-2}$ | | s | | |

# EXTENSIONS

## GROWTH IN A FINITE DOMAIN

- The final fraction of the γ' phase tends toward the equilibrium fraction (reached for 5.7 nm)
- The analytical solution with choice 3 ($[A]^{\sim}$ plain curves with + symbols) follows very well the numerical solution ($[N]^{R_f}$ dashed curves) during the 1st growth regime
- Choice 3 is better than choice 1 ($[A]^{-}$ dashed dot curves) for evaluating the far field composition $\tilde{X}_i^{\infty}$
- An alternate growth/dissolution regime is observed when approaching equilibrium ($D_{inf}$)
- Extension of the Laplace solution for a full diffusion matrix is used for dissolution as the analytical solution is only valid for growth
- The alternate growth/dissolution regime is also computed with the analytical solution but it differs from the numerical one

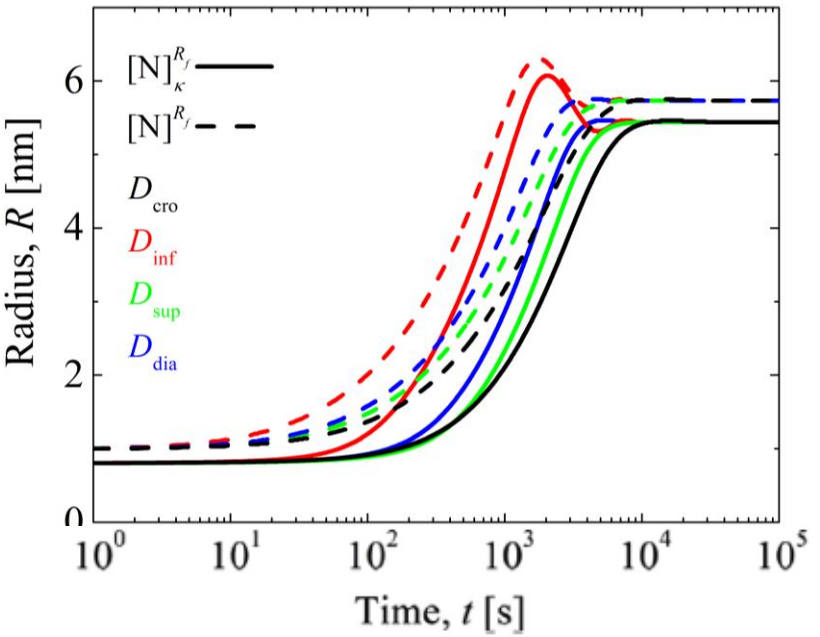


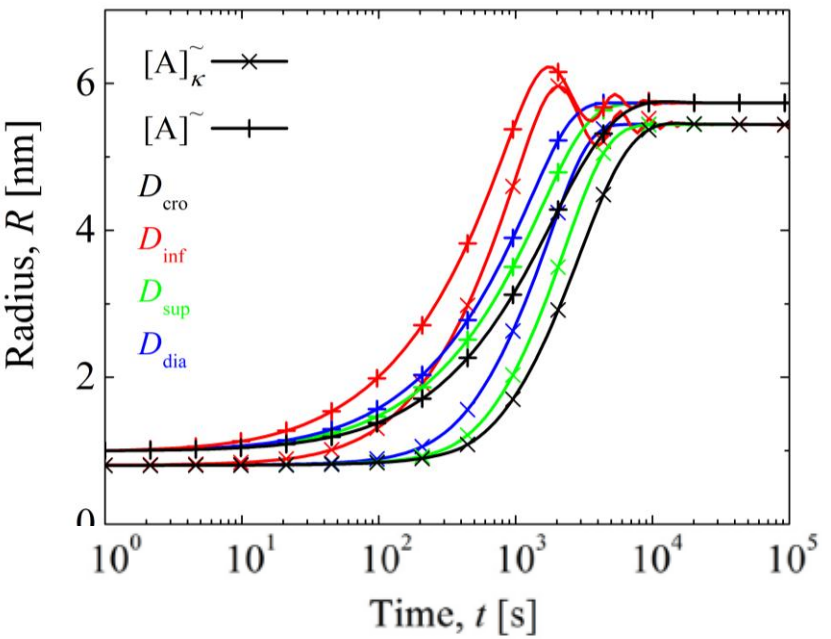
# EXTENSIONS

## EFFECT OF CURVATURE

- Curvature ($[N]_{\kappa}^{R_f}$ plain curves) delays the growth process for all diffusion matrices
- The equilibrium volume fraction is smaller
- The alternate growth/dissolution regime is kept when approaching equilibrium




- The same delay of the growth process is observed with the analytical solution including curvature ($[A]_{\kappa}^{\sim}$ plain curves with × symbols)
- The analytical solution follows very well the numerical solution accounting for curvature, except for the frequency of the oscillation (due to the Laplace approximation for the dissolution regime)



# CONCLUSIONS

- An analytical solution is developed to compute the interface velocity and the composition profiles with cross diffusion between species in an infinite matrix phase during growth of a single spherical precipitate [GUILLEMOT GANDIN, Acta Mater. 97 (2015) 419].
- Validations are achieved by comparison with numerical solutions.
- The CHEN et al. [Acta Mater. 56 (2008) 1890] growth model, also used in ROUGIER et al. [Acta Mater. 61 (2013) 6396] [Metall. Mater. Trans. 47A (2016) 5557], is not recommended.
- Extensions of the analytical model include
  - Method to approximate the far field composition when considering a finite size spherical domain (i.e. interaction with other precipitates),
  - Laplace solution with cross diffusion used to approximate the dissolution regime (not presented above),
  - Method to handle the curvature effect.
- An oscillation regime is observed, with intensity depending on the diffusion matrix.

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Full length article

# An analytical model with interaction between species for growth and dissolution of precipitates

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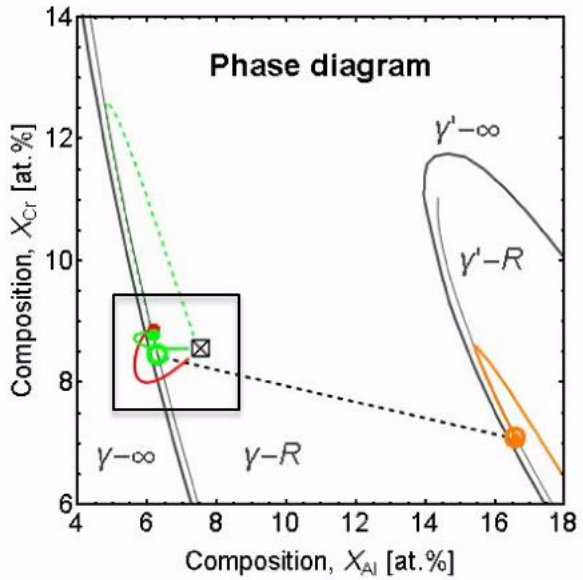
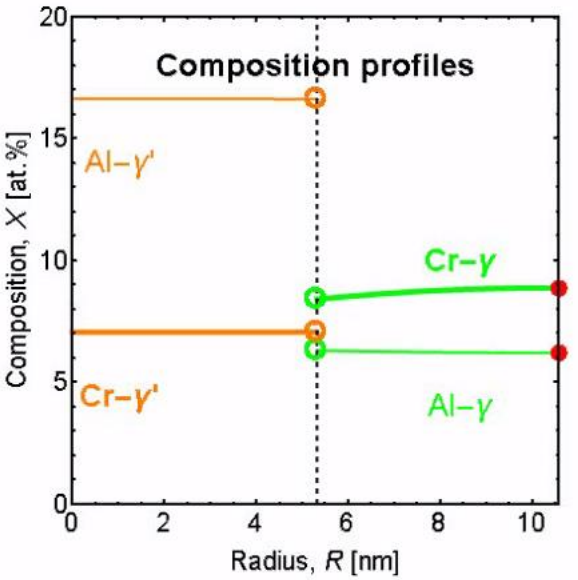
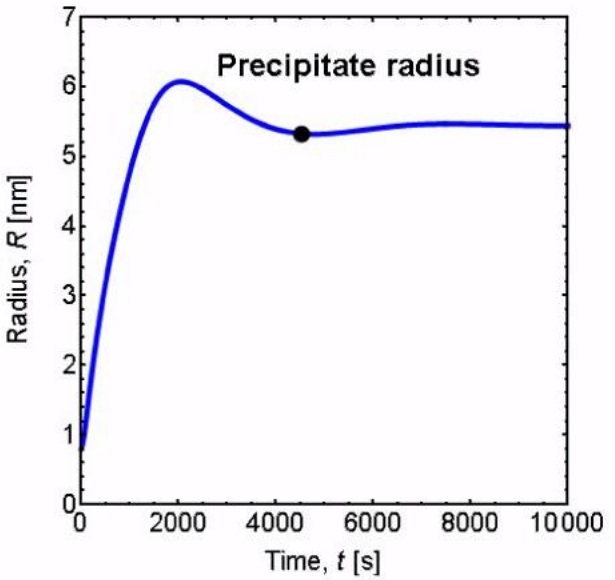
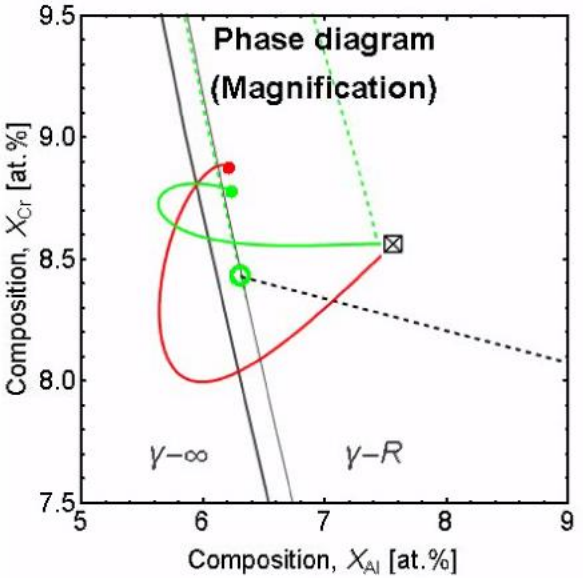
ABSTRACT

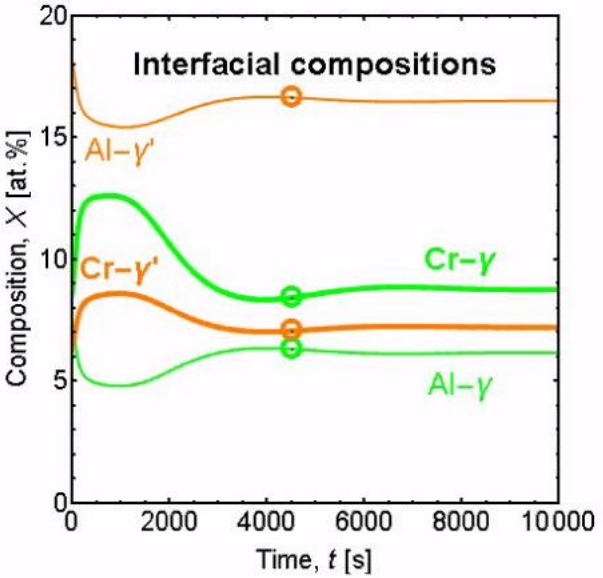
An analytical model for growth in a semi-infinite matrix with cross-diffusion between species is presented. Application is given for precipitation of the γ′-phase in the γ-matrix during isothermal holding at 600 °C in the Ni - 7.56 at.% Al - 8.56 at.% Cr alloy. The exact time-dependent solutions for the solute profiles and the growth kinetics are validated with a numerical front-tracking simulation. The simulation of cross diffusion terms in a multicomponent alloy is thus demonstrated. Extension of the analytical solution is given for growth in a matrix of finite size. The driving force is then based on a mathematical estimation of the far-field composition. The Gibbs-Thomson effect is also accounted for to consider the effect of curvature on the equilibrium tie-lines. Comparison of analytical solution with the numerical front-tracking simulation shows excellent agreement. Results also point out the detrimental approximation of using the average composition of the matrix for computing the driving force as well as the limitation of the solution proposed by Chen et al. [Acta Mater. 56 (2008) 1890]. A detailed discussion is finally given on the origin of oscillations observed for the time evolution of the precipitate radius which alternates between growth and dissolution regimes, pointing out the combined role of solute fluxes and tie-lines compositions at the precipitate/matrix interface.

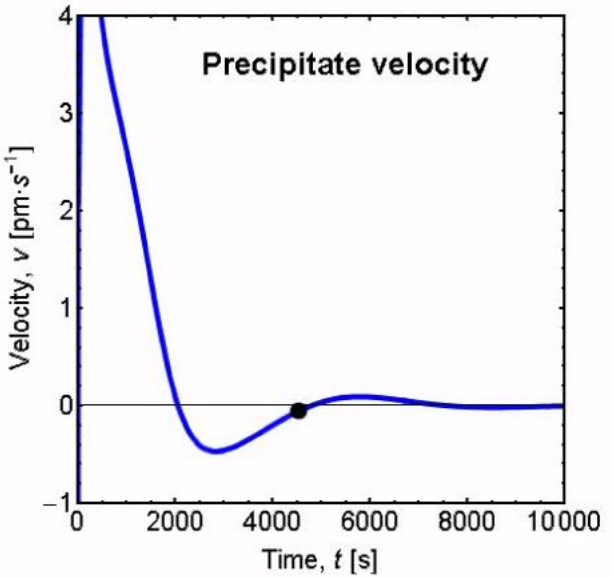



γ – matrix ● average / ○ interface

γ' – precipitate ● average / ○ interface

⊠ alloy ● boundary ● current time

$t$ = 4520. s

$R$ = 5.32 nm

$v$ = –0.0594 pm·s$^{-1}$