

# Improved Design of Nano-Composites through Parameter Leveraging

<sup>[1]</sup> Rahul Basu

Professor, Adarsha Institute of Technology  
Off Intl Airport Road, Kundana, Bangalore 561120

**Abstract:-** Composites have been used for many applications seeing use in the Construction, Automotive and Aerospace Industries. The emergence of nano-materials has permitted the design of new materials like nanocomposites. These have interfaces at molecular length scales and large interaction areas. In particular, the area to the volume ratio is higher which permits the tuning of volume fraction of secondary components without loss of desired properties. New areas of design can use chemical and phase chemistry along with electrical electronic and mechanical properties. The effect of secondary contributions on the design of fracture resistant nano composites is outlined.

**Keywords:-** Nano-composites; fracture; toughness; phase transformations

## I. INTRODUCTION

Nucleation and growth in Metallurgy and phase change is well known and studied for at least 50 years. The first attempts at controlling morphology for technological purposes were with the attempts at directional solidification, applied to unidirectional composites and in situ turbine blades by the aerospace industry. These efforts were dominated by the use of thermal and concentration control. NASA had dedicated research programs to investigate the growth of precipitates in Ni superalloys, Lemkey [1975]. With the advent of nanotechnology, a variety of techniques have been applied to get preferred morphologies. Efforts for control of surface texture, potential and ultrasound have been proposed Cvelbar, Hee, Hoytot, [ 2007-2011 ]. Another area is in the phase field approach where models are used to simulate nucleation and preferred morphology for dendritic growth, Granasy [ 2006 ]. However in the area of castings, Chvorinov [1940] postulated the effect of volume and surface area on the solidification time of castings, which indicates the relative effect of surface to volume ratios and should be effective even at smaller levels from physical principles. Carslaw & Jaeger [1959] have given solutions to many of the standard thermal problems. However, the solutions of the Mass diffusion equation and the coupled Heat and mass diffusion equation are less well known. In particular, solutions of the MBP for concentration based problems were not tackled by Carslaw & Jaeger. Paterson (1954) lists solutions for various geometries in the case of the thermal diffusion equation,

using erf( $\eta$ ), cylindrical  $Ei(\eta)$ , and in spherical coordinates, the spherical error function. The matrix is a system with numerous pathways for movement of the mass components and may be described by the effective diffusion coefficient D. In effect the matrix is a porous system, given a porosity  $\epsilon$ . In order to solve the mass diffusion equation, we assume idealized quantities for the boundary condition. Let the concentration far away from the mass source be  $C_0$ , and that as the encapsulated liquid be  $C_1$ . By a transformation, these may be reduced to 0 and  $(C_1 - C_0)$ . The diffusion equation may be written as

$$D \frac{d^2 C}{dx^2} = \frac{dc}{dt}$$

$$C(x=0, t) = C_1 - C_0, \quad C(x=\infty, t) = 0 \quad [1]$$

If the mass at  $x=0$  is limited then there is no continuous source, and these boundary conditions suffice to get a solution since this is a second order equation and only two conditions are sufficient for a solution.

Transforming to similarity variables:  $D \frac{d^2 C}{d\eta^2} = \frac{dc}{d\eta}$ , where  $\eta$  is a similarity variable

In various coordinate systems, the solution is obtained as:

$$C = A + B \operatorname{erf}(\eta) \quad [2]$$

$$C = E + F Ei(\eta) \quad [3]$$

$$C = L + M \operatorname{spherf}(\eta) \quad [4]$$

The boundary conditions for the linear error function employ

$$\operatorname{erf}(0) = 0, \quad \operatorname{erf}(\infty) = 1$$

$$C = A = 0, \quad \text{when } x=0, \quad B = (C_1 - C_0), \quad x = \infty \quad [5]$$

$$\text{Hence } C(\eta) = (C_1 - C_0) \operatorname{erf}(\eta)$$

Similarly for the spherical case, at infinity,  $\operatorname{spherf}(\infty) = 0$

And a similar relation holds

However in the cylindrical case,  $Ei(0)$  has a singularity at the origin

Comment [G2]: Deleted:c

Comment [G1]: Inserted: ,

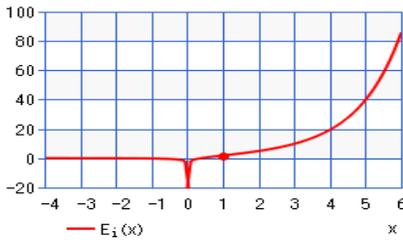


Figure 1: Graph showing singularity of  $E_i$

**3. Method**

The method of simulation consists of formulating the equations for the two phases and then setting up a mass balance at the interface. The balance is then solved assuming equilibrium at the moving interface which constitutes a moving boundary problem.

**3.1 In the case of the spherical geometry,**

An artifice is used to reduce it to the one-dimensional case, as given by Crank, (1959).

Let  $C=U/r$ , then the concentration diffusion equation transforms to the familiar one dim case, the solutions of which can be written:

$$(C-C_0)/(C_1-C_0) = (a/r) \operatorname{erfc}(r-a)/2\sqrt{\pi Dt} \quad [6]$$

The boundary condition at  $r=0$  is avoided.

Where  $C_0$  is the initial concentration at  $r>a$ , and  $r=a$  maintained at  $C_1$ . If one keeps to finite radii and avoids the singularities at the origin, these three scenarios can be represented by these formulae. In the present case, let us look at the spherical case: By means of the transform  $U = Cr$ , both the spherical and rectilinear cases can be represented by the erf formula, with the small change that for the spherical case, the erf is divided by  $r$ .

The output of the erf and the erf/r functions is  $C = c_0 + (c_1 - c_0) \operatorname{erf}(h)$  [7]

$$C = c_0 + (c_1 - c_0) (a/r) \operatorname{erf}\{(r-a)/2\sqrt{\pi Dt}\}, a=0.1 \quad [8]$$

The two functions can be illustrated by a plot of the differences:

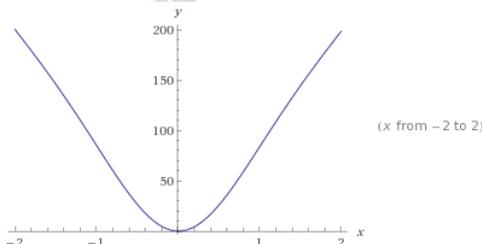


Figure 2: difference (erf - erf/r)

It is obvious that the concentration from the spherical case is greater than that from the rectilinear, due to the appearance of  $r$  in the denominator of the second function. We can conclude that diffusion from a sphere is much faster than that from a 1D or 2 D source. Similarly, it can be shown that diffusion from a sphere is faster than that from a cylinder.

3.1 Specific solution for 1-D Moving Boundary system: Following Carslaw Jaeger [1959], the problem is formulated in terms of mass diffusivities and applying a jump condition across the interface where chemical reaction has occurred, where  $\alpha$  is the un reacted phase,  $\beta$  the reacted phase. Paterson (1952) lists solution for the thermal diffusion problem with moving boundaries of the phase transformation.

The equations are

$$D^\beta \frac{\partial c^\beta}{\partial x} - D^\alpha \frac{\partial c^\alpha}{\partial x} = (c^{\alpha*} - c^{\beta*}) \frac{d\xi}{dt} \quad [9]$$

Where although activities are equal across the equilibrium interface, the concentrations are assumed unequal, ie there is a jump.

$$c^\alpha(x, t) = \frac{c^{\alpha*}}{1 + \operatorname{erf}(\lambda)} \left[ 1 + \operatorname{erf}\left(\frac{x}{2\sqrt{D^\alpha t}}\right) \right]$$

$$c^\beta(x, t) = \frac{1}{\operatorname{erfc}(\lambda/\psi^{1/2})} \left[ c^{\beta*} - \operatorname{erf}(\lambda/\psi^{1/2}) + (1 - c^{\beta*}) \operatorname{erf}\left(\frac{x}{2\sqrt{D^\beta t}}\right) \right] \quad [10]$$

$$\frac{c_0 - c^{\beta*}}{\lambda\sqrt{\pi}\operatorname{erf}(\lambda)} e^{-\lambda^2} - \frac{(c^{\alpha*} - c_1)e^{-\lambda^2\psi}}{\sqrt{\pi}\lambda\psi^{1/2}\operatorname{erfc}(\lambda\psi^{1/2})} = c^{\beta*} - c^{\alpha*} \quad [12]$$

Geometry	Heat sink	adiabatic
Cylindrical	0.0669	0
Spherical	0.09763	-0.01607

Where RHS is the jump in concentration across the reacting interface,

$$\xi(t) = 2\lambda\sqrt{D^\beta t} \quad \psi = \frac{D^\beta}{D^\alpha} \quad [13]$$

$$\xi(t) = 2\lambda\sqrt{D^\beta t} \quad [14]$$

Interface position:  
The solutions for each side of the moving boundary can be obtained from the above.

Comment [G5]: Inserted: (1952)

Comment [G3]: Inserted: -

Comment [G4]: Inserted: entration

### 3a SURFACE-VOLUME CONSIDERATIONS

In physical metallurgy Chvorinov's rule gives the time for cooling a casting in terms of its volume and surface areas. Using the abbreviated form of the rule

Time for solidification is found from  
 $t = \text{Const}(V/A)^2$  [15]

Calculation of the V/A ratios for a thin plate, cylinder and sphere gives:

V/A plate =  $L/2$  where  $h/L \ll 1$  [16]

V/A cylinder =  $L/2(1+L/R)$  [17]

V/A sphere =  $R/3$  [18]

It can be seen that if L/R is small for the cylinder, the plate and cylinder become equivalent, whereas if  $L/R \sim 1$  the cylinder has smallest time V/A ratio for  $R=L$ , while if  $R < L$ , the sphere has smaller ratio

In fact if the velocity of the moving boundary is calculated for various geometries, it is found that the sphere, cylinder and plate have different velocities. The time to solidify would be directly related to the velocity. A series approach was attempted by Soward (1980) where the velocities of spherical and cylindrical freezing were compared.

For identical parameters, the velocity of spherical is found to be higher than that of cylindrical, Basu(2015)

Table 1: comparisons of rates for various conditions

It should be noted however, that these rates deal with long or infinite cylinders, since the end effects are not considered.

### II. CONCLUSIONS

Considerable work has been done over the past few decades on control of precipitation and coarsening in alloys by use of phase temperature control. Such control mainly dealt with macro structures where uncontrolled dendritic growth occurred with time. In the above, an attempt has been made to illustrate the parameters that control the development of such macrostructures starting from the microstructures at the nano level. Through proper leveraging of the various parameters, the morphologies and size of the precipitates can be controlled, resulting in uniform morphologies and thereby better control of physical and mechanical properties.

### REFERENCES

1. Basu R, (2015) "Freezing and Sublimation Under Various Boundary Conditions for Cylinders and Spheres", Prof of Intl Conf on Materials and Mfg Tech, ICMMT-2015, (Dec3-5,2015), Mc Graw Hill,p101-109
2. Carslaw Jaeger (1959), "Conduction of Heat in Solids", OUP

3. Crank J, (2009) "The mathematics of diffusion", OUP
4. Chvorinov N,(1940),"Theorie die Erstarung von Gusstucken", Giesseret, 27,10 pp 177-188
5. Cvelbar U, Ostrikov K, Levchenko I "Control of morphology and nucleation density of iron oxide nanostructures by electric conditions on iron surfaces exposed to reactive oxygen plasmas" Appl. Phys. Lett. 94, 211502 (2009); doi: <http://dx.doi.org/10.1063/1.3147193>
6. Gang Hee Han, Fethullah Güneş, Jung Jun Bae Influence of Copper Morphology in Forming Nucleation Seeds for Graphene Growth, Nano Lett., 2011, 11 (10), pp 4144-4148DOI: 10.1021/nl201980
7. Granasy L, Puzstai C, Borzonyi T "Phase Field Theory of Nucleation and Polycrystalline Pattern Formation", Handbook of Theoretical and Computational Nanotechnology Edited by Michael Rieth and Wolfram Schommers American Scientific Publishers, Stevenson Ranch, CAL, 2006 Volume 9: Pages (525-572)
8. Hottot A, Nakagawa K, J Andrieu J"Effect of ultrasound-controlled nucleation on structural and morphological properties of freeze-dried mannitol solutions", <http://dx.doi.org/10.1016/j.cherd.2007.11.009>
9. Lemkey FD, McCarthy GP,"Quaternary and quinary modifications of the eutectic superalloy gamma/gamma prime-delta", NASA, Conference on In Situ Composites, 2nd, Bolton Landing, N.Y., September 2-5, 1975, Proceedings. (A76-43301 22-24) Lexington, Mass., Xerox Individualized Publishing, 1976, p. 77-87; Discussion, p. 87, 88
10. Paterson S (1952) "Propagation of a boundary of fusion", Proc of Glasgow Math Assn, v1, pp42-47
11. Soward AM, (1980), "A unified approach to Stefan's Problem for spheres and cylinders", doi 10.1098/rspa.1980.0140
12. Tao A R, Habas S, Yang P,(2008), "Shape Control of Colloidal Metal Nanocrystals", DOI: 10.1002/sml.200701295, small, 4, No. 3, 310 – 325

### Nomenclature

A area  
 A,B, C constants  
 c concentration  
 D diffusion coefficient  
 Ei Exponential integral function  
 Erf error function  
 E elastic modulus  
 $\alpha, \beta$  labels for the interacting phases  
 K conductivity

**Comment [G6]:** Inserted: Ei Exponential integral function

**Comment [G7]:** Inserted: Erf error function

**Comment [G8]:** Inserted: E elastic modulus

K<sub>ic</sub> fracture toughness parameter

L length

R radius

T time

V volume

$\lambda$  eigenvalue for interface velocity

$\psi$  ratio of diffusivities

$\tau$  time

$\xi$  similarity parameter solved for velocity  $\lambda$

**Comment [G9]:** Inserted: K<sub>ic</sub> fracture toughness parameter

**Comment [G10]:** Inserted: K conductivity

