A Study of the Mass Transfer Kinetics during the Dissolution of Ti-N Particles in Liquid Titanium

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Abstract. This paper summarizes the development of a computational fluid dynamics (CFD) model based on the commercial software package ANSYS-CFX, which has been used to examine the kinetics of dissolution of a single stationary Ti-N particle surrounded by moving liquid titanium. The model accounts for diffusional mass transport in the solid particle, the formation of a two-phase solid/liquid boundary layer and both advective and diffusional transport to the bulk liquid. The results have been used to estimate an effective mass transfer coefficient that may be applied in models that only consider solid-state mass transport of nitrogen. The results show that a correction is needed to the conventional Ranz-Marshall correlation to more accurately calculate the mass transfer coefficient during the Ti-N particle dissolution process.

1. Introduction
The Electron Beam Cold Hearth Remelting (EBCHR) and Plasma Arc Melting (PAM) processes have been developed to produce premium quality titanium for applications in the aerospace industry. These processes are designed to remove a variety of inclusions including hard-alpha (Ti-N) particles using a combination of dissolution and density separation. Dissolution, the focus of this work, relies on solute mass transport to drop the melting temperature of the particle to below or at the local temperature of the fluid. Therefore, understanding the dissolution kinetics of Ti-N particle inclusions in liquid titanium is important for the purpose of process design.

Previous studies have shown that the dissolution of Ti-N particles in liquid titanium alloys is strongly affected by the particle composition (N content), temperature, residence time and the velocity of the particle relative to the fluid [1-3].

In this work, a CFD model was developed to examine the kinetics of dissolution of a single stationary Ti-N particle within flowing liquid titanium. The model was developed using the commercial CFD software package ANSYS-CFX.

2. Model description
The CFD particle dissolution model was developed using the multicomponent flow solver available in ANSYS-CFX (v15.0). The model is assumed isothermal with a constant temperature of 1700°C. The multicomponent model consists of two components: nitrogen (solute) and liquid titanium (solvent).
2.1 Governing equations
Since the model is isothermal the energy conservation equation is not solved. The governing partial differential equations describing mass conservation and momentum conservation are presented in Equations (1) and (2):

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{1}
\]

\[
\frac{\partial \rho \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \rho \mathbf{u} = \nabla \cdot \mathbf{\tau} - \nabla \mathbf{p} + \mathbf{S}_M \tag{2}
\]

where \( \rho \) (kg·m\(^{-3}\)) is the density, \( t \) (s) is time, \( \mathbf{u} \) (m·s\(^{-1}\)) is the velocity vector, \( \mu \) (Pa·s) is the viscosity, \( \mathbf{\tau} \) (N·m\(^{-2}\)) is the shear stress tensor, \( \mathbf{p} \) (N·m\(^{-2}\)) is the pressure force vector.

ANSYS-CFX [5] solves Equations (1) and (2) for the entire domain including the “solid” Ti-N particle. In order to suppress flow within the solid material, the dynamic viscosity is ramped linearly with increasing solid fraction from 0.003 Pa·s in the liquid [6] to 3 Pa·s in the solid. In addition, a flow dampening term \( \mathbf{S}_M \) was added based on Darcy’s law. Both approaches were found to be necessary to fully curtail flow in the solid.

The compositional transport equation that calculates mass transport of solute (nitrogen) is shown in Equation (3):

\[
\frac{\partial \rho m_N}{\partial t} + \nabla \cdot \rho m_N \mathbf{u} = D_N \nabla^2 \rho m_N \tag{3}
\]

where \( m_N \) is the mass fraction of nitrogen, and \( D_N \) (m·s\(^{-2}\)) is the diffusivity of nitrogen in titanium. The material properties, such as liquid viscosity, diffusivity and density, used in the model are summarized in Table 1[3,6].

2.2 Mesh and geometry
The dimensions of the domain used in the model are 6mm × 6mm × 18mm as shown in Figure 1(a). Liquid titanium flows into the domain from the left side surface (Inlet in Figure 1(a)) and out of the domain from the right surface (Outlet in Figure 1(a)). A cross-sectional view of the mesh, normal to the flow direction, is shown in Figure 1 (b). The initial radius of the particle is assumed to be 1mm.

![Figure 1](image_url)

**Figure 1.** Geometry of the computational domain (a) and cross-sectional view of the mesh (b) used in the model.

2.3 Initial and boundary conditions
As would be expected from the Ti-N phase diagram – see Figure 2 – \( \alpha \)-Ti (HCP) and \( \beta \)-Ti (BCC) may be expected to be present within the particle at 1700°C dependent on the nitrogen content. Assuming an initial nitrogen content of 5wt% for the bulk of the particle, the solid particle would start as pure \( \alpha \)-Ti
due to the stabilizing effect of the N. As the nitrogen is removed from the particle surface, the \( \alpha \)-Ti would be expected to transform to \( \beta \)-Ti. In the model a small layer of \( \beta \)-Ti, 10\( \mu \)m in thickness is assumed to be present initially in order to setup the appropriate boundary conditions. The various phase boundary interfaces are assumed to be at equilibrium. The interface compositions and diffusivity for the various phases are given in Table 1, see also Figure 2 (b). The bulk fluid is assumed to initially contain no nitrogen. At the inlet boundary, the fluid velocity is set equal to the slip velocity of the particle. A free slip adiabatic wall boundary condition is applied to all the other surfaces of the domain.

![Figure 2](image)

**Figure 2.** Thermodynamic phase diagram of Ti-N (a) and replot (b) of the zoom-in area around the temperature 1700°C used in the model [7].

|                  | Phase \( \alpha \) | Phase \( \beta \) | Liquid            |
|------------------|---------------------|-------------------|------------------|
| Initial radius/thickness (m) | \( 10^{-3} \) | \( 10^{-5} \) | --               |
| Equilibrium N mass fraction at phase boundaries | 0.035@ \( \alpha/\alpha\beta \) | 0.017@ \( \alpha\beta/\beta \) | 0.0015@ \( \beta/\beta\)l |
| Initial N mass fraction | 0.05 | 0.015 | 0               |
| Viscosity (Pa·s) | 3 | 3 in \( \beta \); 0.003-3 in \( \beta\)l | 0.003[6] |
| Diffusivity (m²·s⁻¹) [2] | \( 3.1 \times 10^{-3} \exp\left( -\frac{168 \times 10^3}{RT} \right) \) | \( 4.6 \times 10^{-1} \exp\left( -\frac{185 \times 10^3}{RT} \right) \) | \( 5.13 \times 10^{-9} \) |
| Density (kg·m⁻³) [3] | 4520 | 4370 | 4100            |
| Slip velocity (m·s⁻¹) | 0.005 - 0.1 | 0.005 - 0.1 | 0.005 - 0.1 |
| Temperature (°C) | 1700 | 1700 | 1700            |
3. Results and discussions

3.1 Nitrogen concentration profile
Figure 3 shows the calculated nitrogen concentration profile in the liquid and particle, and the fluid velocity vectors on the cross-sectional plane at various simulation times during particle dissolution. The black outline highlights the solid particle areas surrounded by the β/βl interface. It is shown that the particle does not keep its spherical shape as it dissolves. The surface facing upstream is preferentially eroded by the incoming fluid due to the enhanced convective mass transfer.

![Figure 3](image)

(a) Nitrogen concentration profile (contour) and fluid velocity (vectors) at the cross-sectional plane at (a) 30s, and (b) 120s predicted by the particle dissolution model (slip velocity = 0.01 m·s⁻¹).

3.2 Evolution of particle size during dissolution
Figure 4 shows the evolution of the radius of the particle estimated with the model for a series of different slip velocities. Initially, the diffusion rate to the particle/liquid interface is higher than the transport rate from the particle/liquid interface, causing the particle to grow, which is observed in all the cases examined.

![Figure 4](image)

Figure 4. Evolution of the particle radius predicted at four different slip velocities.

The result shows a range of dissolution times from 30s, for a slip velocity of 0.1 m·s⁻¹, to in excess of a 160s, for a slip velocity of 0.005 m·s⁻¹. Obviously, prediction of dissolution times in an industrial setting will hinge on a good understanding of slip velocities experienced by a typical particle in an
3.3 Effective mass transfer coefficient

An effective mass transfer coefficient, \( MTC_e \), has been calculated based on the result of the particle dissolution model, using the following expression [8]:

\[
MTC_e = \frac{(m_N^t - m_N^{t-\Delta t})}{A \cdot \Delta t \cdot (C_{\beta} \rho_\beta - C_l \rho_l)}
\]  \( (4) \)

where \( m_N^t \) (kg) is the total mass of nitrogen within the particle at the current time step \( t \); \( \Delta t \) (s) is the time step size; \( A \) (m\(^2\)) is the surface area of the particle; \( C_{\beta} \) is the equilibrium nitrogen mass fraction at the \( \beta/\beta+l \) interface and \( C_l \) is the nitrogen mass fraction in the bulk liquid; and \( \rho_\beta \) (kg·m\(^{-3}\)) and \( \rho_l \) (kg·m\(^{-3}\)) are the densities of \( \beta \) and bulk liquid, respectively.

The effective mass transfer coefficient was calculated at the four slip velocities and has been plotted as solid lines in Figure 5(a), together with the \( MTC \) estimated using the Ranz-Marshall correlation for the various slip velocities, plotted as the dashed lines. The results show that the effective \( MTC_e \) calculated from the CFD dissolution model follows the same trends as the \( MTC \) predicted by the Ranz-Marshall correlation – i.e. the variation in mass transfer coefficient with slip velocity and particle radius. However, there is an appreciable difference, with the Ranz-Marshall correlation tending to over predict the mass transfer coefficient, particularly for the lower slip velocities examined. Potential reasons for this have been examined, but not presented here for sake of brevity.

To offset the difference, a “tuning” coefficient, \( k \), has been proposed for the Ranz-Marshall correlation to bring it into alignment with the effective \( MTC_e \) predicted by the CFD model – i.e. \( MTC_e = k \cdot MTC \). Figure 5 (b) shows a comparison between the CFD-based \( MTC_e \) and the result for the tuned Ranz-Marshall relationship. The fitting coefficients are presented as a function of the slip velocities in Figure 6, together with a linear equation describing the dependence of \( MTC_e \) on \( v_{slip} \). At the highest slip velocity studied in this work, \( v_{slip} = 0.1 \) m·s\(^{-1}\), the fitting coefficient is one, meaning the unmodified Ranz-Marshall correlation is applicable.

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**Figure 5.** Comparison of the effective mass transfer coefficient calculated by the CFD particle dissolution model and the original Ranz-Marshall correlation (a) and modified Ranz-Marshall correlation (b).
Figure 6. Coefficients used to correct Ranz-Marshall correlation for the effective mass transfer coefficient.

4. Conclusions
A CFD particle dissolution model has been developed to predict the dissolution time of a Ti-N particle in liquid titanium. The effect of particle/fluid slip velocity was assessed. The results show that the dissolution time decreases as the slip velocity increases. The effective mass transfer coefficient was estimated based on the CFD model’s predictions and compared with the conventional Ranz-Marshall correlation. The result shows that a correction is needed to the Ranz-Marshall correlation to more accurately describe the mass transfer kinetics during the Ti-N particle dissolution process, particularly at lower slip velocities.

References
[1] Bellot J P, Foster B, Hans S, Hess E, Ablitzer D and Mitchell A 1997 Metall. and Mater. Trans. B 28B 1001
[2] Ghazal G, Jardy A, Chapelle P, and Millet Y 2010 Metall. and Mater. Trans. B 41B 646
[3] Ghazal G, thesis: Etude de la Propreté Inclusionnaire des Lingots VAR - Application aux Alliages de Titane, Institut Jean Lamour, Département SI2M, CNRS-Nancy-Universite-UPVM, Ecole des Mines, Parc de Saurupt, 54042 Nancy Cedex, France, 2010
[4] Ranz W E and Marshall Jr. W R 1952 Chem. Eng. Prog. 48 141.
[5] ANSYS CFX-Solver Theory Guide, release 15.0, ANSYS Inc., PA November 2013
[6] I.C. Mills 2002 Recommended Values of Thermophysical Properties for Selected Commercial Alloys, Woodhead, Cambridge, England
[7] Wriedt H A and Murray J L 1986 Binary Alloy Phase Diagrams vol 3, eds Massalski T B(ASM) p 2705
[8] Ou J, Chatterjee A, Cockcroft S, Maijer D, Reilly C, and Yao L 2015 Int. J. Heat Mass Transf. 80 386