

A comparison of the pseudo-steady-state and shrinking-core model for the reduction of titanium dioxide to titanium

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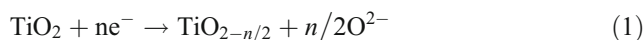
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Abstract A multistage shrinking-core model is proposed for the electrodeoxidation of titanium dioxide to titanium. This takes place through a series of steps from TiO_2 to Ti_3O_5 to Ti_2O_3 to TiO to Ti . Ideally, the model would incorporate a number of shells of the above lower oxide phases with the shrinking core of TiO_2 in the center but this would be mathematically intractable. A simpler method would be to use the shrinking-core model for each of the individual reductions. Taking the experimental parameters and diffusion coefficient of oxygen in the different phases into account, an analytical solution is developed for the transient differential equation. The first ten eigenvalues are taken into account for the computation of the series solution. This is then compared with a solution based on a pseudo-steady-state approximation to the transient equations. Based on the results, for higher values (>0.01) of dimensionless applied current density, I_d , both the solutions disagree in terms of the time it takes for the core to shrink completely. The difference appears to be decreasing with lower values of I_d but for larger values of I_d the pseudo-steady-state approximation fails to yield results close to the analytical solution.

Keywords Diffusion (C) · Computer simulations (D) · Metals and alloys (A)

Introduction

The Fray–Farthing–Chen (FFC) process [1–15] of titanium extraction is a novel electrochemical method for extracting titanium from titanium dioxide. It is being investigated for possible commercialization in the US and in Europe for the reduction of titanium dioxide to titanium as well as for the reduction of other metals and alloys (Metalysis Inc., <http://www.metalysis.com/markets.htm>).



In the FFC process for reducing titanium, pressed and sintered pellets of TiO_2 are made the cathode in an electrochemical cell with a carbon anode and molten CaCl_2 electrolyte at 900–950 °C. The overall reduction for the FFC process occurs via the reaction in Eq. 1 and proceeds through successive lower oxides from TiO_2 in a sequence of $\text{TiO}_2 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}[\text{O}] \rightarrow \text{Ti}$ [13–15]. At a granular level, this can be explained as a shrinking core of TiO_2 with a lower oxide from one of the above forming in the shell. A multistep shrinking-core formulation incorporating each of these steps would be an ideal model for the reaction and would yield insight on the effect of parameters like the current density, radius of the grains, and diffusion coefficients on the reduction. It has been shown in some prior experimental work that perovskite phases (CaTiO_3) form during the reduction of TiO_2 depending on the activity of the oxygen ions [16–18]. One of the significant assumptions of this modeling work is that oxygen is present at unit activity in the pores of the pellet (outside the grains composing the pellet). With this assumption, the perovskite formation can be neglected.

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A shrinking-core formulation has been used by Pritzker [19] for modeling the movement of reaction front during multispecies uptake onto an ion-exchange resin. He has shown that at relatively lower counter-ion concentrations the pseudo-steady-state and transient solutions are relatively close to each other. At larger concentrations, the pseudo-steady-state approximation is found to be less valid. Zhang and Ostrovski [20] have used a shrinking-core formulation for a kinetic model of titanium dioxide reduction by a methane–hydrogen–argon gas mixture. They have calculated the activation energies and kinetic parameters for the reduction reactions using a shrinking-core model. Bayramoglu and Tekin [21] have used the shrinking-core model to study the reduction kinetics during the electrochemical reduction of manganese dioxide with ferrous ions. They have obtained the values of charge transfer coefficients and also the order of the cathodic reduction reaction.

For the reduction of TiO_2 , a shrinking-core model is implemented for each of the reaction steps shown in

Table 1. The first step is for the reduction of TiO_2 to Ti_3O_5 , the second step for Ti_3O_5 to Ti_2O_3 , the third being Ti_2O_3 to TiO , and the final step being TiO to Ti . The parameters of significance of each of these steps are the diffusion coefficients of oxygen in each of the above phases, the applied current density, the radius of the grains, and the density of the phases. Taking the case of step 1 in Table 1, the initial concentration of oxygen in the solid phase is C_{TiO_2} . Upon reduction, the region of the grain close to the exterior gets depleted of oxygen resulting in the formation of an oxygen-deficient shell of Ti_3O_5 with a concentration of $C_{\text{Ti}_3\text{O}_5, s1}$. The concentration of oxygen at the interface is obtained from the phase diagram and is termed $C_{\text{Ti}_3\text{O}_5}$. A comparison is made for the regimes of validity of the pseudo-steady-state case and for the transient case. The insight gained from this modeling work is used for the implementation of a pellet level model of the FFC process that also uses the shrinking-core formulation.

Table 1 The four steps in the reduction of TiO_2 to Ti

Steps	Reactions
Step - I	
Step - II	
Step - III	
Step - IV	

Model development

Prior to the start of reduction, in the solid phase of the cathode, all the grains are TiO₂. Once reduction starts, the exterior of the grain gets depleted of oxygen forming a shell of a lower oxide of titanium (Ti₃O₅) as shown in Fig. 1. As reaction proceeds, the shell of Ti₃O₅ grows inwards while the core of TiO₂ shrinks resulting in a classical shrinking-core type of reaction.

For the scenario presented in Fig. 1, the concentration of oxygen ions in the reduced oxide phase (in this case Ti₃O₅) is given by

$$\frac{\partial c}{\partial t} = \frac{D_{Ti_3O_5}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \tag{2}$$

Where *c* = concentration of oxygen ions (moles per cubic centimeter), *t* = time (seconds), *D*_{Ti₃O₅} = diffusion coefficient of oxygen ions in Ti₃O₅ (m²/s).

The initial condition is known (completely unreacted TiO₂)

$$\begin{aligned} c &= c_{TiO_2} \\ t = 0, 0 \leq r \leq r_p \end{aligned} \tag{3}$$

and the boundary conditions are

$$D_{Ti_3O_5} \frac{\partial c}{\partial r} = -\frac{i}{nF} \tag{4}$$

at *r* = *r_p* with *t* > 0, where *F* is Faraday’s constant, 96,450 C/mol, *i* is the applied current density at the surface (A/m²), *r_p* is the radius of the particles (m), and *D*_{Ti₃O₅} is the diffusion coefficient of the oxygen ion in the Ti₃O₅ phase (m²/s).

The boundary condition for Eq. 4 suggests that the driving force for diffusion is directly dependent on the applied current density.

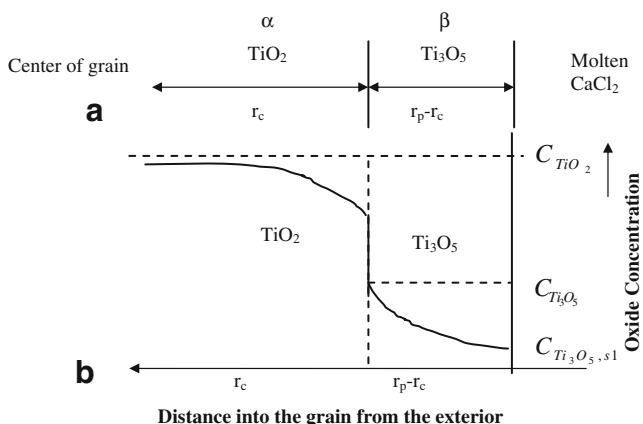


Fig. 1 a A sketch of the situation at the Ti₃O₅–TiO₂ interface during the reduction, b expected concentration profiles in the solid

The concentration at the Ti₃O₅–TiO₂ moving interface could be obtained from the phase diagram and is a constant.

$$c = c_{Ti_3O_5} \tag{5}$$

at *r* = *r_c* with *t* > 0

The movement of the interface is governed by the mass flux due to the electrochemical reaction at the interface and is given by the following equation

$$(c_{TiO_2} - c_{Ti_3O_5}) \frac{\partial r_c}{\partial t} = D_{Ti_3O_5} \frac{\partial c}{\partial r} \tag{6}$$

with the differential at the right hand side of Eq. 6 being evaluated at *r* = *r_c*.

The above formulation (Eqs. 2–6) can be nondimensionalized by using the following dimensionless variables for distance (dimensionless interface position and dimensionless radial distance)

$$x = \frac{r}{r_p}; \quad x_c = \frac{r_c}{r_p} \tag{7}$$

Similarly, for time, we can introduce a dimensionless time

$$\tau = \frac{D_{Ti_3O_5} t}{r_p^2} \tag{8}$$

and a dimensionless concentration

$$c^* = \frac{c}{c_{Ti_3O_5}} \tag{9}$$

Eq. 2 with its initial and boundary conditions changes to Eq. 10.

$$\left(\frac{1}{x^2} \right) \frac{\partial}{\partial x} \left(\frac{\partial c^*}{\partial x} \right) = \frac{\partial c^*}{\partial \tau}$$

$$\begin{aligned} c^* &= 0; \quad \tau = 0 \\ c^* &= 1; \quad x = 1 \\ \frac{\partial c^*}{\partial x} &= -I_d; \quad x = x_c \quad \text{where} \end{aligned} \tag{10}$$

$$I_d = \frac{iR}{FD_{Ti_3O_5} c_{Ti_3O_5}}$$

The interface position is given by

$$\frac{\partial x_c}{\partial \tau} = -\gamma \frac{\partial c^*}{\partial x} \tag{11}$$

where $\gamma = \frac{1}{c_{TiO_2}^* - 1} = \frac{1}{\frac{c_{TiO_2}}{c_{Ti_3O_5}} - 1}$ is a dimensionless constant.

For each of the shrinking core at different stages of the reaction, the above Eq. 10 can be solved to yield an analytical expression for the concentration as a function of position and time. The analytical solution for the above

equations can be obtained by using a separation of variable method [22–24] that results in a solution of the form,

$$c^*(x, \tau) = u(x, \tau) + w(x) \tag{12}$$

where

$$w(x) = 1 + I_d \left(\frac{1}{x} - \frac{1}{x_c} \right) \tag{13}$$

$$u(x, \tau) = \frac{1}{x} \sum_{n=1}^{\infty} A_n \sin(\lambda_n[x - x_c]) \exp(-\lambda_n^2 \tau) \tag{14}$$

where λ'_n s are the eigenvalues that are evaluated from the transcendental equation $\tan(\lambda_n[1-x_c]) = \lambda_n$, $n=1, 2, \dots$ and $A_n(n=1, 2, \dots, \infty)$ are constants and are calculated by imposing initial conditions on the differential equation yielding Eq. 14.

Incorporating the expressions for $w(x)$ and $u(x, \tau)$ into Eq. 12, we have the expression describing the concentration of oxygen ions as shown in Eq. 15.

$$c^*(x, \tau) = 1 + I_d \left(\frac{1}{x} - \frac{1}{x_c} \right) - \frac{2}{x} \left(\sum_{n=1}^{\infty} A_n \sin(\lambda_n(x - x_c)) \exp(-\lambda_n^2 \tau) \right) \tag{15}$$

where $A_n = \frac{x_c \gamma + I_d \cos(\lambda_n(1-x_c))}{\lambda_n(x_c - \sin^2[\lambda_n(1-x_c)])}$

For obtaining the pseudo-steady-state solution, the left-hand side of Eq. 2 is set to 0 and the resulting expression integrated. This, yields Eq. 16 for the concentration.

$$C_{\text{surface}} = 1 + I_d \left(\frac{1}{x} - \frac{1}{x_c} \right) \tag{16}$$

Using Eq. 16 and solving Eq. 11 yields the expression for x_c as in Eq. 17

$$x_c = (1 - 3\gamma I_d \tau)^{1/3} \tag{17}$$

The above equations were solved by writing a script in Matlab™ 7.0 and results for the dimensionless interface position were obtained for both the transient and pseudo-steady-state solution.

Results and discussion

The first ten eigenvalues are computed by solving the transcendental equation mentioned earlier ($\tan(\lambda_n[1-x_c]) = \lambda_n$, $n=1, 2, \dots, \infty$) to yield values of the λ'_n s as a function of x_c . The eigenvalues are plotted with x_c ranging from 0 to 0.99 as shown in Fig. 2. The values are typically high at higher x_c values and low at lower x_c values.

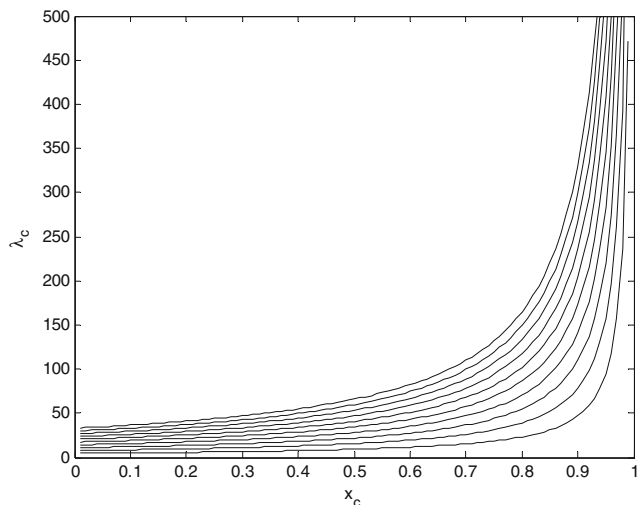


Fig. 2 A plot of the first ten eigenvalues as a function of x_c

The values of x_c are obtained by integrating Eq. 11 using the explicit time-stepping approach shown in Eq. 18

$$x_c(\tau + \Delta\tau) = x_c(\tau) + \Delta\tau \left[\gamma \frac{\partial c}{\partial x} \Big|_{x=x_c} \right] \tag{18}$$

where $x_c=1$ at the start of the reduction and is reduced to 0 at the end of reduction. The concentration gradient in Eq. 18 is obtained by differentiating the expression for the concentration in Eq. 15. This yields the values for the position of the interface boundary as a function of the dimensionless time for each of the reactions based on the values of the parameters shown in Table 2.

The interface position shows the movement of the boundary between the reduced and the unreduced phase. For the reduction of TiO_2 to Ti_3O_5 , the solution based on the full transient solutions is shown in Fig. 3. As expected, for higher current densities (increasing I_d values), the time for the reduction decreases. The dimensionless applied current density was varied from 0.01 to 2.01 in increments of 0.1 for all the four reduction reactions. A similar trend is also observed for the pseudo-steady-state approximation as shown in Fig. 4. For this case, the pseudo-steady-state

Table 2 Diffusion coefficients (cm^2/s), Oxygen concentration in titanium oxides and the current densities during each state of reduction

Phase	Diffusion coefficient (cm^2/s) [16]	Oxygen concentration in the lower oxides	Current density during the reduction (A/g)
TiO_2	2.6×10^{-5} [26]	2	–
Ti_3O_5	8.24×10^{-9} [25]	1.66	0.3
Ti_2O_3	9.14×10^{-9} [25]	1.5	0.05
TiO	8.3×10^{-8} [26]	1	0.02
Ti	10^{-10} [26]	0	0.01

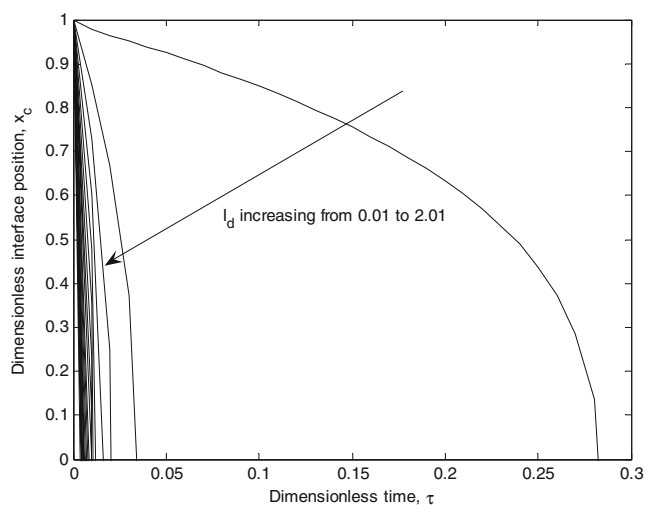


Fig. 3 Dimensionless interface position as a function of dimensionless time showing the times based on the transient solution for reaction TiO_2 to Ti_3O_5 . The time required for the core to completely shrink decreases with increasing values of the dimensionless applied current density

approximation overpredicts the time taken for all of the I_d values used in the computations ranging from 0.01 to 2.01. As will be shown later, these values are closest to one set of experiments reported in the literature.

A trend similar to the reduction of TiO_2 to Ti_3O_5 is seen for the reduction of Ti_3O_5 to Ti_2O_3 as shown in Figs. 5 and 6 and the reduction of Ti_2O_3 to TiO as shown in Figs. 7 and 8. In both of these cases, the pseudo-steady-state solution disagrees with the transient solution for the completion of the shrinking core.

For the last reaction for the reduction of TiO to Ti , the transient (Fig. 9) and the steady-state (Fig. 10) solutions

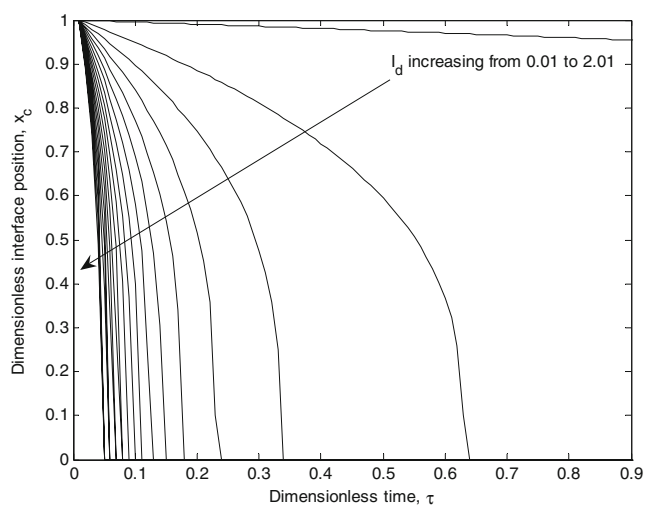


Fig. 4 Dimensionless interface position as a function of dimensionless time showing the times based on the pseudo-steady-state solution for reaction TiO_2 to Ti_3O_5 . The pseudo-steady-state solution overpredicts the time required for the core to reduce completely

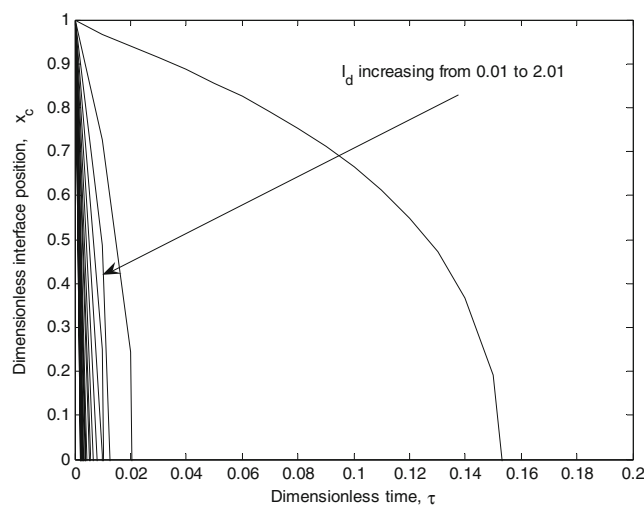


Fig. 5 Dimensionless interface position as a function of dimensionless time showing the times based on the transient solution for reaction Ti_3O_5 to Ti_2O_3

also do not agree and the pseudo-steady-state solution underpredicts the time for the complete shrinking of the core for all values of I_d used for the calculations. Similar observations were made by Pritzker [19] for the reaction fronts in their paper on multispecies uptake onto an ion-exchange resin.

As discussed earlier, for all of the above reductions, the pseudo-steady-state and the transient solution disagree with each other to different extents in each of the cases. But on close comparison of all the transient and pseudo-steady-state solutions, it seems that they tend towards agreement for lower values of I_d . Based on this observation, for modeling the complete process on a pellet level and finally on a reactor level, the value of I_d must be calculated for

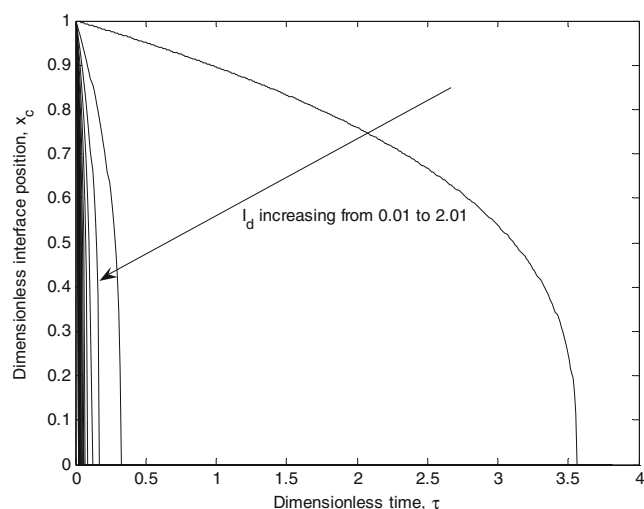


Fig. 6 Dimensionless interface position as a function of dimensionless time showing the times based on the pseudo-steady-state solution for reaction Ti_3O_5 to Ti_2O_3

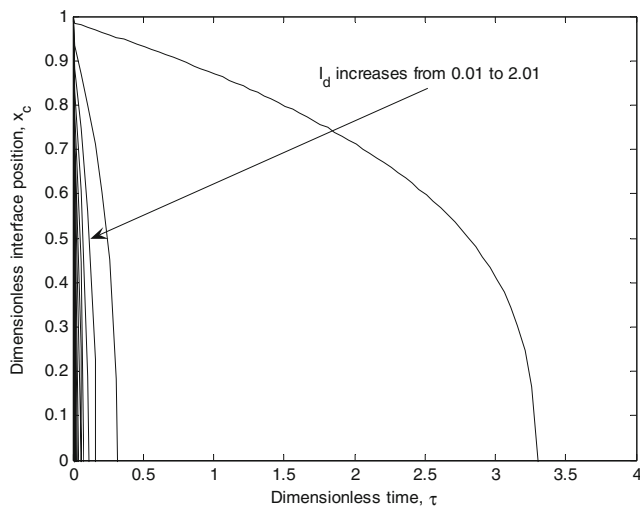


Fig. 7 Dimensionless interface position as a function of dimensionless time showing the times based on the transient solution for reaction Ti_2O_3 to TiO

each of the reduction reactions. The value of I_d depends on a number of factors, namely the applied current, the radius of the particles or the average grain size after sintering, and the value of the diffusion coefficient of oxygen in each of the lower oxide phases.

Based on the values reported by Schwandt and Fray [16] for one set of experiments, the value of I_d for the reaction of TiO_2 to Ti_3O_5 is 0.0008, for the reaction of Ti_3O_5 to Ti_2O_3 is 0.0001, for the reaction of Ti_2O_3 to TiO is 6.98×10^{-6} , and for the reduction of TiO to Ti is 0.0043. For modeling this particular set of experiments, one could conveniently use the pseudo-steady-state solution for the reduction of the higher oxide phases because the I_d values are low enough and would result in similar solutions for the steady-state and the transient formulations.

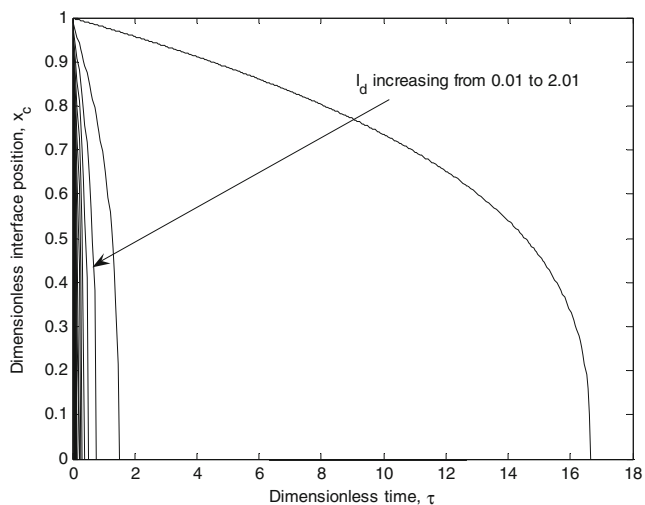


Fig. 8 Dimensionless interface position as a function of dimensionless time showing the times based on the pseudo-steady-state solution for reaction Ti_2O_3 to TiO

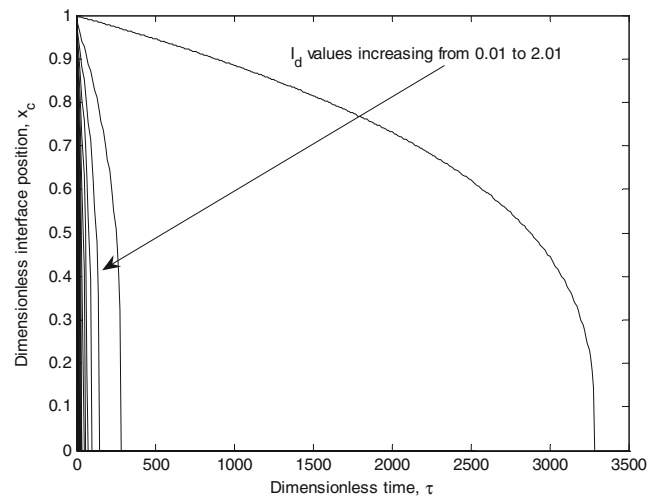


Fig. 9 Dimensionless interface position as a function of dimensionless time showing the times based on the transient solution for reaction TiO to Ti

Conclusion

A multistage shrinking-core model is proposed for the reduction of the titanium oxides to titanium based on the FFC process. A transient solution and a pseudo-steady-state solution are developed for each of the stages of the reduction. This yields valuable insight on whether the pseudo-steady-state approximation can be used without compromising accuracy. This information can be used for a reactor scale model incorporating the shrinking-core reduction and this model can be used for solving other multistage processes involving the shrinking core. The formulation could be potentially applied to solid-state batteries having phase change electrodes and would yield the regimes of operation at different discharge rates.

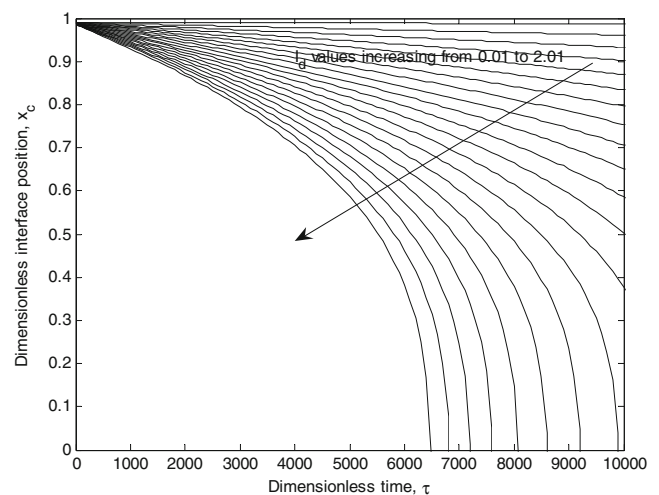


Fig. 10 Dimensionless interface position as a function of dimensionless time showing the times based on the pseudo-steady-state solution for reaction TiO to Ti

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