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The combustion synthesis of refractory nitrides

Part 1 *Theoretical analysis*

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A theoretical analysis of the formation of refractory metal nitrides through the combustion of metal powders in a nitrogen atmosphere is presented. Thermodynamic and kinetic criteria are employed to determine the dependence of the process on the nitrogen pressure and on the porosity of the compacts. For metals which can dissolve large amounts of nitrogen, the relative contributions of the processes of nitrogen dissolution and nitride phase formation are analysed.

1. Introduction

The concept of preparing compounds through the propagation of a wave in a gasless combustion process was first proposed more than three decades ago [1] and has since found practical applications in the synthesis of a large number of metallic and ceramic phases [2]. The underlying thermodynamic principle for this process is a large exothermic reaction enthalpy capable of sustaining the reaction in the form of a combustion wave moving through the reactant mixture. When used for the preparation of materials, such a process is termed self-propagating high-temperature synthesis (SHS) or simply combustion synthesis. Interest in this process as an alternative method for the preparation of materials has been largely motivated by the potential for low cost production and by assertions of uniqueness in the properties of materials prepared by this process.

In nearly all cases, solid materials (typically powders) are mixed and ignited. However, when preparing nitrides, the reaction is commonly between a solid and nitrogen gas, and thus the criteria of gasless combustion are not valid in this case. In principle the dependence of the combustion process on the pressure of the nitrogen gas can be evaluated from thermodynamic considerations. However, the process can be complicated by kinetic limitations arising from the interaction between the solid (e.g. a metal) and molecular nitrogen to form a nitride or a solid solution of nitrogen in the metal. Although nitrides can be prepared by the combustion of metals in liquid nitrogen or by the combustion of a mixture of the metal and an azide [3], we will focus in this paper on nitride synthesis through solid–gas combustion reactions. In a subsequent paper we will present results of experimental investigations on the formation of nitrides.

2. Thermodynamic considerations

Thermodynamic calculations provide information on the minimum nitrogen pressure required to form the nitride phase, and thus give a lower limit for the required nitrogen pressure under which the nitride is stable. For the reaction between a metal, M, and nitrogen gas to form a nitride MN, i.e.

$$\mathrm{M}(s) + 1/2\mathrm{N}_2(g) = \mathrm{MN}(s) \qquad (1)$$

the minimum nitrogen pressure, P_{N_2}, for the spontaneous formation of the phase MN is

$$P_{\mathrm{N}_2} = \exp\left(\frac{2\Delta G^0}{RT}\right) \qquad (2)$$

where ΔG^0 is the Gibbs' free energy of formation of the nitride, T is the absolute temperature, and R is the universal gas constant. Values of P_{N_2} calculated for selected nitrides are shown in Fig. 1 as log P_{N_2} against $1/T$. As can be seen from this figure, even at relatively high temperatures (e.g. 2000 K), these nitrides can be formed in the presence of nitrogen gas at one atmosphere pressure. Obviously higher pressures are needed at higher temperatures and thus, the choice of the latter parameter (T) is of primary concern when attempting to determine whether or not a given metal (element) will form a nitride. In this regard two temperatures are of concern in combustion synthesis: the ignition temperature, T_{ig}, and the adiabatic temperature, T_{ad}. The former is the temperature at which the reaction is initiated and the combustion front begins to propagate while the latter is the maximum temperature to which the product will be heated under adiabatic conditions [4]. Thus, the nitrogen pressure of interest in the combustion synthesis of nitrides lies in the range corresponding to temperatures between T_{ig} and T_{ad}. However, unlike the adiabatic temperature, the ignition temperature cannot be calculated

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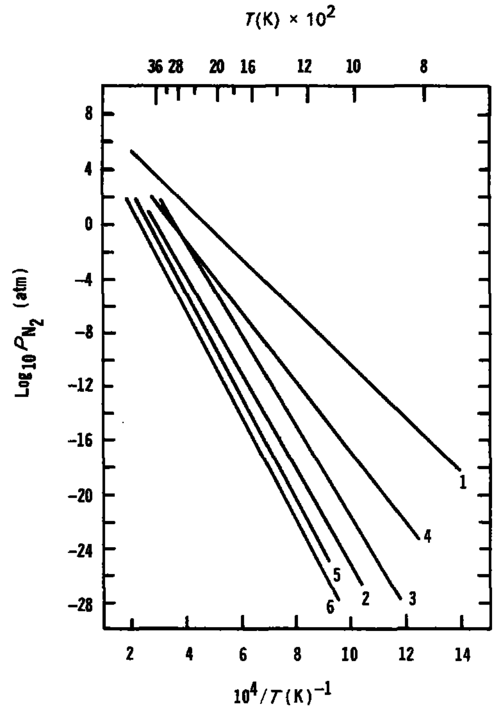

Figure 1 Equilibrium dissociation pressures of nitrogen, P_{N_2}, for selected nitrides. 1, Si_3N_4; 2, TiN; 3, AlN; 4, BN; 5, ZrN; 6, HfN.

from thermodynamic principles and must be determined experimentally for each system. For this reason P_{N_2} values are calculated as a function of a normalized temperature, T/T_{ad}, as shown in Fig. 2, for the range $0.4 \leqslant T/T_{ad} \leqslant 1.0$. At the highest temperature in this range, i.e. at $T/T_{ad} = 1.0$, the equilibrium nitrogen pressures vary over a relatively wide range for the nitrides shown in Fig. 2. The values of P_{N_2} at this temperature are approximately 1, 10^2 and 10^5 atm for AlN, BN and Si_3N_4, respectively.

Experimental observations on the dependence of nitride formation on P_{N_2} have shown that much higher pressures than the equilibrium values are required to ignite these elements [5]. This observation suggests the existence of an activation energy, whose genesis can be chemical or mass-transport in nature. For our purpose here, chemical activation energies are those related to the reaction rate theory. Activation energies connected with the atomic diffusion of nitrogen through a product layer or with the permeation of molecular nitrogen through powder compacts are examples of mass-transport activation energies. A discussion of both types of activation energies is presented in the following section.

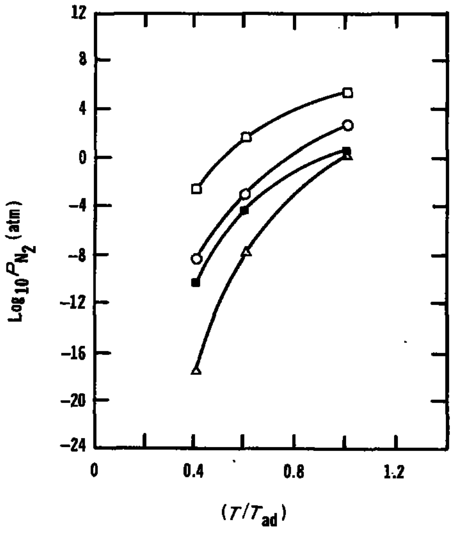

Figure 2 Equilibrium nitrogen pressures as functions of the normalized temperature, T/T_{ad}. □, Si_3N_4; ○, BN; ■, TaN: △, AlN.

3. Kinetic considerations

The degree of conversion to a nitride for metallic particles located in the interior of a powder compact depends on the local availability of nitrogen. Larger and more numerous pores in the compact favour higher degrees of conversion and lower dependence on the permeation of the nitrogen gas through the compact. Ideally, a combustion process will be independent of permeation of the gas if the amount of nitrogen occupying the total volume of pores is that which is stoichiometrically required for the total conversion to the nitride. For a given compact porosity, this amount is of course a function of the temperature and pressure of the nitrogen gas. We define the parameter C as the degree of conversion i.e.

$$C = \frac{1}{S}\left(\frac{m_{N_2}}{m_M}\right) \tag{3}$$

where m_{N_2} and m_M are the number of moles per unit volume of nitrogen gas and the metal, respectively, and S is the stoichiometric ratio, i.e. the number of moles of N_2 per mole of metal in the reaction. For example $S = 1/2$ for a reaction such as that represented by Equation 1. According to Equation 3 and assuming $S = 1/2$, permeation is not required for complete conversion ($C = 1$) if there are two moles of metal for every mole of N_2 gas occupying the pores. Assuming ideal gas behaviour for nitrogen and substituting for the molar numbers, Equation 3 becomes

$$C = \frac{1}{S}\left[\frac{P_{N_2\varepsilon}}{RT}\bigg/\frac{(1-\varepsilon)\varrho}{A}\right] \tag{4}$$

which simplifies to

$$C = \frac{1}{S}\left[P_{N_2}\cdot\frac{\varepsilon}{(1-\varepsilon)}\cdot\frac{V_m}{RT}\right] \tag{5}$$

where P_{N_2} is the pressure of N_2(g); ε, the porosity of the powder compact; ϱ, the density of the metal; A, the atomic weight of the metal; V_m, the molar volume of the metal; R, the universal gas constant and T the absolute temperature.

Nitrogen pressures corresponding to varying degrees of conversion of Ti to TiN were calculated by means of Equation 5 for three porosity values and two temperatures. The results are shown in Fig. 3. The porosity range was selected to reflect practical upper and lower limits. The upper limit ($\varepsilon = 0.7$) represents a value typical of uncompacted (loose) powders while the lower limit ($\varepsilon = 0.2$) is typical of highly compacted powders which retain continuous open porosity. Fig. 3 shows that in order to obtain complete conversion (i.e. $C = 1$) of Ti to TiN with nitrogen present in pre-existing pores it is necessary to raise P_{N_2} to in excess of 10^3 atm for $\varepsilon = 0.7$ and to in excess of

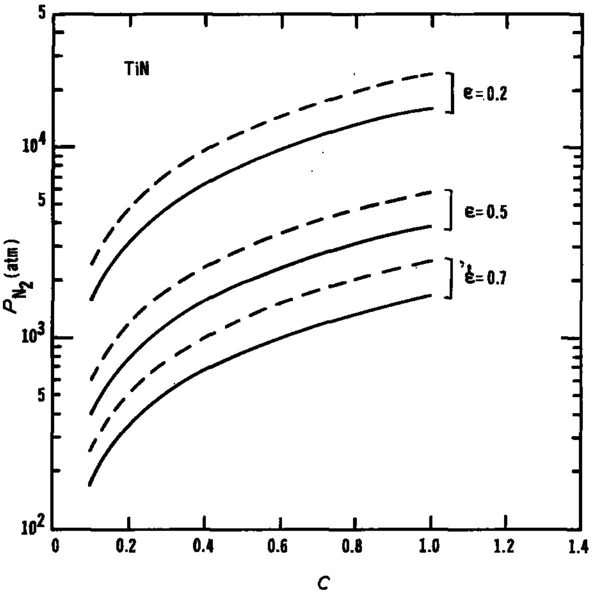

Figure 3 The dependence of the degree of conversion to TiN on the pressure of nitrogen gas in pre-existing pores. ——, $T = 1000$ K; - - -, $T = 1500$ K.

10^4 atm for $\varepsilon = 0.2$. As expected, Fig. 3 shows that for any given porosity and degree of conversion, higher pressures are required at higher temperatures. Fig. 4 shows the relationship between P_{N_2} and C for a selected group of nitrides calculated at $T = 1500$ K and $\varepsilon = 0.7$. A closer examination of Equation 5 reveals that the relative position of any of the curves plotted in Fig. 4 is directly dependent on the molar volume of the metal. Thus, a more explicit relationship demonstrating this point is

$$P_{N_2} = \frac{S(1 - \varepsilon)}{\varepsilon} \cdot \frac{RT}{V_m} \tag{6}$$

Plots of P_{N_2} against V_m for four nitride stoichiometries are shown in Fig. 5 for $T = 1500$ K and $\varepsilon = 0.5$. The stoichiometries chosen, M_3N_4, MN, M_3N_2, M_2N, represent known stable nitrides, examples of which are indicated on the corresponding curves by the element represented by M in the formula. Fig. 5 gives an overview of the relative requirement (in tersm of P_{N_2}) to achieve complete conversion with only the nitrogen present in pre-existing pores in the powder compact. As such, the curves of Fig. 5 serve as an indication of the general trend of susceptibility of the combustion of an element to the problem of permeation. For example, the elements of Zr and Hf would be expected to be less affected by problems of permeation than boron (see Curve B in Fig. 5).

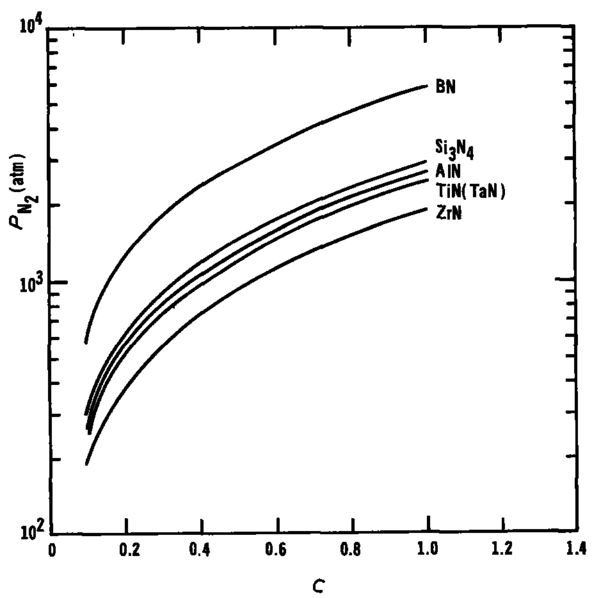

Figure 4 The dependence of the degree of conversion to nitrides on P_{N_2} for selected elements. $T = 1500$ K; $\varepsilon = 0.7$.

According to the preceding analysis, the combustion of a metal is not affected by the permeation of the nitrogen gas if P_{N_2} is equal or higher than that calculated by Equation 6. However, at lower pressures the combustion process may not be controlled by permeation if the rate of flow of N_2 gas through the pores is equal to or greater than that required to sustain the reaction. Experiments relating the nitrogen pressure to some parameters of the combustion process should provide indications of the relative role of permeation. An example of such experiments was provided by the investigation of Barzykin and Stovbun [6] on the combustion of niobium powder compacts in a nitrogen atmosphere. For any given compact porosity, the ignition temperature was found to decrease with increasing nitrogen pressure up to a certain (threshold) P_{N_2} value, and to remain constant with further increase in the pressure. The implication of these observations is that at or above the threshold pressure values, the combustion of niobium is not controlled by the permeation of the nitrogen gas. Since the observed threshold pressures were higher than the equilibrium values at the corresponding ignition temperature, these results imply the existence of an activation energy which is chemical in nature. The value of this activation energy, ΔG^*, can be calculated from

$$\Delta G^* = RT_{ig} \ln \left[\frac{P_{N_2}(\text{obs})}{P_{N_2}(\text{eqm})} \right] \tag{7}$$

where T_{ig} is the ignition temperature, $P_{N_2}(\text{obs})$ and $P_{N_2}(\text{eqm})$ are, respectively, the observed (threshold) and equilibrium pressures at the ignition temperature. Calculations of ΔG^* values were made using the data of the cited study [6] and the results are shown in Fig. 6 as ΔG^* against ε. Extrapolating the linear relationship to the limiting case of $\varepsilon = 1.0$ gives a ΔG^* of 31.4 kcal mol^{-1} as the chemical activation energy for the combustion of niobium powders in a nitrogen gas.

4. Simultaneous formation of nitrides and solid solutions

Implicit in the above considerations is the assumption that the solubility of nitrogen in the metal is negligible and that the nitride phases resulting from combustion are (or nearly) stoichiometric. While this assumption is valid for the formation of nitrides of elements such as aluminium and silicon, it cannot adequately describe the combustion synthesis of a large number of refractory nitrides, notably those of the transition metals. In these cases, the combustion process is complicated by the nature of the phase equilibria between

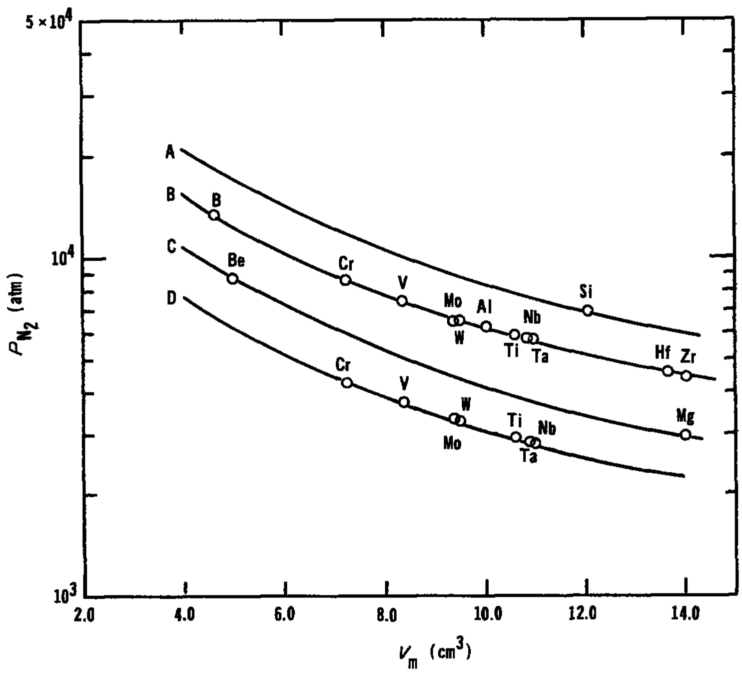

Figure 5 A generalized relationship between P_{N_2} and the molar volume of elements with useful nitrides at complete conversion to the appropriate nitride phase. $T = 1500$ K; $\varepsilon = 0.5$. Nitride phases: A, M_3N_4; B, MN; C, M_3N_4; D, M_2N.

nitrogen and the metals. Transition metals form stable phases of solid solutions of nitrogen which in some cases exist over a wide range of composition. For example, titanium and nitrogen form a solid solution extending up to about 24 at % N [7]. Moreover, the nitrides of the transition metals are highly non-stoichiometric with wide ranges of compositional stability fields. The combustion synthesis of nitrides of transition metals is, therefore, the sum of contributions of two processes: nitride formation and nitrogen dissolution.

A schematic representation of the products of combustion of a transition metal in a nitrogen atmosphere is shown in Fig. 7. The variation of the nitrogen concentration, (C_N) with distance, x, from the gas–solid interface is depicted for a case in which a nitride phase forms on top of a solid solution. In the figure, the concentration profile of nitrogen in a nitride phase of thickness ξ is assumed to be linear but the concentration profile through the underlying metal is represented by [8].

$$C_N = C_0 + B\left[1 - \mathrm{erf}\,\frac{x}{2(D_M t)^{1/2}}\right] \quad (\text{for } x > \xi) \tag{8}$$

where C_0 is the original concentration of nitrogen in the metal, D_M is the diffusion coefficient of nitrogen in the metal, t is time, and B is a constant defined by

$$B = \frac{(C_M - C_0)}{[1 - \mathrm{erf}\,\gamma(D_N/D_M)^{1/2}]} \tag{9}$$

with γ being a constant. Using the analagous case for the oxidation of transition metals [8], we can write the equation for the rate of total weight gain (per unit area) due to the uptake of nitrogen as

$$\begin{aligned}\frac{\mathrm{d}m}{\mathrm{d}t} &= -D_N\left(\frac{\mathrm{d}C_N}{\mathrm{d}x}\right)_{x<\xi}\\ &= (C_i - C_M)\frac{\mathrm{d}\xi}{\mathrm{d}t} - D_M\left(\frac{\mathrm{d}C_N}{\mathrm{d}x}\right)_{x>\xi}\end{aligned} \tag{10}$$

where m is the weight gain per unit area; D_N, the

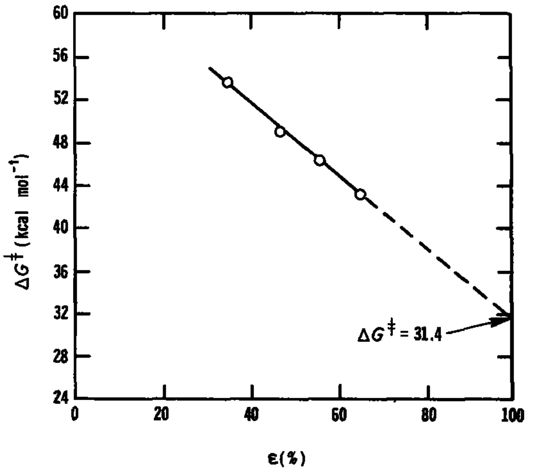

Figure 6 The dependence of the activation energy for the formation of NbN on the porosity of the metal powder compacts.

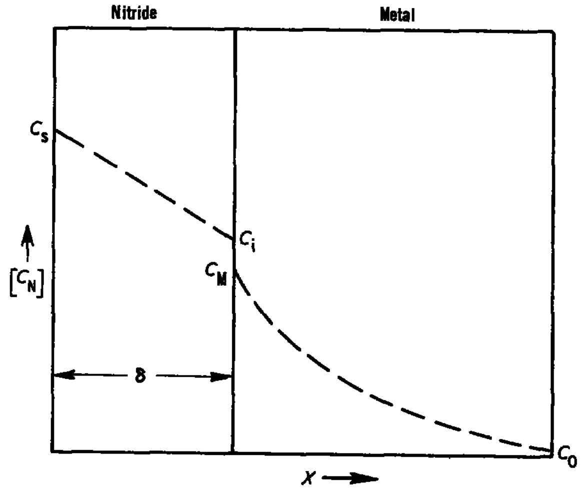

Figure 7 A schematic representation of the formation of a nitride phase and a solid solution of nitrogen in a metal.

diffusion coefficient of nitrogen in the nitride phase; D_M, the diffusion coefficient of nitrogen in the metal; C_i, the equilibrium concentration of nitrogen in the nitride at the nitride–metal interface; C_M, the concentration of nitrogen in a saturated metal solution and t, time.

The second term on the right-hand side of Equation 10 represents the uptake of nitrogen by the metal to form a solid solution. For a finite sample size, this term goes to zero as $C_N \rightarrow C_M$, i.e. as the metal approaches the state of saturation with nitrogen. At this point, the rate of growth of the nitride layer, i.e. $d\xi/dt$ should increase abruptly. The time, τ, at which this occurs for a spherical sample with a radius r is [9]

$$\tau \simeq 0.6 \frac{r^2}{D_M} \qquad (11)$$

where, again, D_M is the diffusion coefficient of nitrogen in the metal. Experimental observations on the interaction between nitrogen gas and heated transition metal wires have demonstrated the occurrence of the abrupt changes in the growth rate of the nitride layer [10, 11]. In the case of Ti and Nb, the rate increased abruptly at some given time, in accordance with theoretical expectations. However, in the case of Zr, the rate $d\xi/dt$ decreased abruptly, in disagreement with the anticipation of Equation 10. The times at which $d\xi/dt$ changed abruptly, τ_{obs}, were found to be in reasonable agreement with those calculated from Equation 11 [5, 10, 11].

Experimental observations on titanium (to be published in a subsequent paper) have shown evidence for the formation of a surface nitride layer and an underlying solid solution of nitrogen in titanium. An approximate calculation of the relative thickness of the nitride phase can be made recognizing that

$$J_N \leqslant J_M \qquad (12)$$

where J_N and J_M are the nitrogen flux through the nitride and metal phases, respectively. Now, if we assume as a rough approximation a time-independent concentration gradient then

$$\frac{\delta_N}{\delta_M} \leqslant \frac{D_N}{D_M} \cdot \frac{(\Delta C)_N}{(\Delta C)_M} \qquad (13)$$

where δ_N and δ_M are the thicknesses of the nitride and metal (solid solution) layers, respectively, D_N and D_M are as defined earlier, and $(\Delta C)_N$ and $(\Delta C)_M$ are the concentration limits across the nitride and metal layers, respectively. This approximate analysis corresponds to a case where the metal is not saturated with nitrogen. The ratios of the thicknesses of TiN and Ti (solid solution) is calculated from phase equilibria information and diffusion data for nitrogen in TiN and in Ti [7, 8]. The ratio at 1941 K (the melting point of Ti) is

$$\frac{\delta_{TiN}}{\delta_{Ti}} \leqslant 0.18 \text{ for } \alpha\text{-Ti}$$
$$\leqslant 2.6 \times 10^{-3} \text{ for } \beta\text{-Ti} \qquad (14)$$

Because of the non-equilibrium nature of the combustion process, calculations were made for both the α and β phases.

As stated above, the usefulness of the approximate relationship of Equation 13 is based on the assumption that the exposure time of the metal to nitrogen at the combustion temperature is less than the time required to saturate the metal with nitrogen, i.e. less than τ of Equation 11. For a powder compact composed of particles with an average radius of 25 μm, τ is calculated to be 25.3 and 2.8 seconds for α and β-Ti, respectively. The relationship between τ and the thickness of the combustion front, x_s, for which the metal particles are completely saturated with nitrogen is

$$x_s = v\tau \qquad (15)$$

where v is the combustion wave velocity.

From experimental observations [12], a typical value of v for the combustion of titanium in a 1 atm pressure of N_2 is 0.2 cm sec^{-1}. This would require x_s to be about 5.1 and 0.6 cm for the cases of α and β-titanium, respectively. In other words the width of a combustion front moving at 0.2 cm s^{-1} must be 5.1 or 0.6 cm to ensure that α or β titanium becomes saturated with nitrogen with the passage of the front at an assumed temperature of 1941 K, the melting point of titanium. Such calculated values of x_s are from nearly one to several orders of magnitude thicker than estimated widths of experimental combustion fronts. This analysis leads to the conclusion that the conversion of titanium to TiN during the passage of the front is relatively minor as predicted by Equation 14 and observed in preliminary experiments on the combustion of titanium powder compacts [12].

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