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Kinetics of high-temperature reaction in titanium–nitrogen system: nonisothermal conditions

Laurent Thiers, Alexander S. Mukasyan, Aleksey Pelekh, Arvind Varma*

Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

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Abstract

The kinetics of rapid high-temperature reaction in titanium–nitrogen (Ti–N_2) system, when it occurs under essentially nonisothermal conditions, are investigated. For this purpose, we utilized a computer-assisted electrothermography (CAE) set-up built in our laboratory. It is shown that under certain conditions, overshooting occurs where the reaction temperature exceeds the setpoint value. This phenomenon may be considered as self-ignition of the metal in nitrogen and its characteristics (e.g. rate of heat release, maximum temperature, etc.) depend strongly on preheating rate. This effect is explained by change in surface area of the solid reactant during preheating period: lower preheating rates to the setpoint temperature provide more change in the metal reactant microstructure (primarily reduction of specific surface area), which decreases the rate of subsequent chemical interaction. Also, it is found that activation energy, E_a, measured under nonisothermal conditions ($E_a = 330$ kJ/mol) is significantly higher than that obtained from isothermal experiments ($E_a = 210$ kJ/mol). The conclusion is made that isothermal kinetics may in general not be applicable for the nonisothermal case. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium–nitrogen system; Nonisothermal; Self-ignition

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1. Introduction

The goal of the present work is to study the influence of preheating rate on the kinetics of gas–solid reactions, taking the titanium–nitrogen (Ti–N_2) system as an example. This problem is important because in a majority of chemical engineering processes, the reaction system should be preheated before it reaches isothermal conditions or it operates under conditions where temperature changes with time. Some qualitative results available in the literature indicate that heating-time history of the reactants may influence the kinetics of chemical reactions [1–3]. Thus, it is critical to know: (i) to what extent does the behavior of the reaction system depend on preheating rate; (ii) whether one can use kinetics obtained under isothermal conditions to describe the reaction occurring essentially nonisothermally.

By comparing kinetic data obtained using different preheating rates, one may clarify these issues and identify more precise approaches to control the reaction process. For this purpose, in this work, we utilized a computer-assisted electrothermography (CAE) set-up built in our laboratory [4] and described in next section. Note that the same technique was used in our previous related studies [5,6]. For the Ti–N_2 system, it was shown that in the temperature range 1350–1600 K, isothermal reaction kinetics follow a parabolic rate law, corresponding to a sharp-interface model with nitrogen diffusion through the developing titanium nitride layer as the rate controlling step. The obtained activation energy value ($E_a = 210$ kJ/mol) is in good agreement with data available in the literature (218–224 kJ/mol) for diffusion of N_2 in TiN [7–9]. In addition, the influence of preheating rate (to desired reference temperature, T_r) on kinetics of high-temperature reactions under isothermal conditions (at $T = T_r$) was investigated for Nb–N_2 and Ti–N_2 systems in the temperature range 2100–2500 and 1350–1600 K, respectively [6]. The results showed that for both cases, reaction kinetics are enhanced by increasing the preheating rate. Analysis of the experimental data shows that the activation energy of the diffusion coefficient does not depend on preheating rate, while the pre-exponential factor is affected.

During these studies, we also found that at higher temperatures 1600–1900 K and high preheating rates, the process of titanium nitridation occurs in a qualitatively different manner. A so-called overshooting occurs, where the reaction temperature exceeds T_r, and one cannot control the behavior of the system [5]. In the present work, this phenomenon is investigated in detail. It is shown that overshooting may

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* Corresponding author. Tel.: +1-219-631-6491; fax: +1-219-631-8366.
E-mail address: avarma@nd.edu (A. Varma).

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Nomenclature

c	concentration, mol/m^3
c_0	concentration at the surface of the wire, mol/m^3
c_P	heat capacity, J/K mol
D	diffusion coefficient, m^2/s
D_0	pre-exponential factor in the diffusion coefficient, m^2/s
E_a	activation energy, J/mol
h	rate of heat loss, J/s
ΔH	reaction enthalpy, J/mol
L	wire length, m
M	amount of solid reacted, mol
p	rate of heat generation by electric current, J/s
q	rate of heat generation by chemical reaction, J/s
Q	cumulative heat generated by chemical reaction, J
r	radial position in wire, m
r_0	wire radius, m
r_c	position of the reaction interface, m
R	universal gas constant
t	time, s
T	temperature, K
U	voltage, V

Greek Letters

ρ	molar density, mol/m^3
ω	preheating rate, K/s

Subscripts

m	maximum
mp, Ti	melting point of Ti
r	reference

be considered as self-ignition of the metal in nitrogen and its characteristics (e.g. rate of heat release, maximum temperature, etc.) depend strongly on preheating rate. The latter is explained by change in surface area of the solid reactant during preheating period. Also, based on measured temperature–time history, kinetics of nitridation in the ignition mode were calculated. It is found that activation energy measured under essentially nonisothermal conditions is significantly higher than that obtained from isothermal experiments.

2. Experimental

The principal apparatus used during this investigation is a CAE set-up that was designed specifically to determine the intrinsic kinetics of reactions under conditions of high-temperatures and various preheating rates. Although, the technique has been described in detail elsewhere [4], a brief explanation is given below. A schematic diagram of the experimental set-up is shown in Fig. 1. The solid reactant is a 100 μm diameter titanium wire (Electronic Space Products International, 99.97% purity; $T_{\mathrm{mp,Ti}} = 1948$ K), which is placed in the reaction chamber under a steady flow of gaseous reactant (oxygen-free nitrogen, <0.5 ppm O_2). The wire is heated uniformly to reference temperatures (T_r) in the range 1100–1800 K, by applying electric current. The temperature is measured by a photodiode, which is calibrated using a two-color pyrometer (Ircon MR-OR10-99C).

The heart of the set-up is a high-speed temperature controller that allows one to reach high preheating rates, ω up to 4.10^5 K/s, as well as to keep the wire temperature constant at desired T_r (constant temperature regime). The latter is provided by a feedback loop in the electrical circuit of the controller. Specifically, the photodiode signal is amplified and compared with a preset reference voltage, U_r, corresponding to T_r, if the former is higher (lower) than U_r, then the voltage applied to the wire decreases (increases), leading to a temperature reduction (increase). A computer with data acquisition board collects the following parameters as a function of time: temperature, applied voltage and current. Knowing these data together with the rate of heat loss, which is determined independently, one may calculate the rate of heat generation (q) and cumulative heat produced by chemical reaction (Q) as functions of time (see [5] for details). Further, assuming a specific model of chemical interaction, the kinetic parameters of the investigated process can be extracted (Section 3 for an example).

Finally, the microstructures, phase and elemental compositions of cross-sections and surfaces of wires were determined by different methods including Scanning Electron Microscopy (JSM 6400, JEOL), X-ray diffraction (X1 Advanced Diffraction System, Scintag Inc.) and energy dispersive X-ray microanalysis (SIGMA, Kevex).

3. Results

As mentioned previously, it was observed [5] that under some conditions in the Ti–N_2 system, an overshooting occurs, i.e. when the wire reaches the reference temperature (T_r), even though the temperature controller responds fast (within 1 ms), the temperature keeps increasing and exceeds the setpoint (see Fig. 2a). Note that during this period, since the photodiode signal exceeds U_r, no electric power is supplied to the wire. However, it appears that overshooting is controlled by the preheating rate (Fig. 2a). For example, in the case of $T_r = 1840$ K, when $\omega = 1.4 \times 10^4$ K/s, no overshooting is detected, while for $\omega = 1.5 \times 10^5$ K/s, overshooting is observed with maximum temperature $T_m = 1890$ K, which exceeds T_r, but is lower than melting point of titanium $T_{\mathrm{mp,Ti}}$. Further increase of preheating rate to 3.9×10^5 K/s results in longer overshooting with

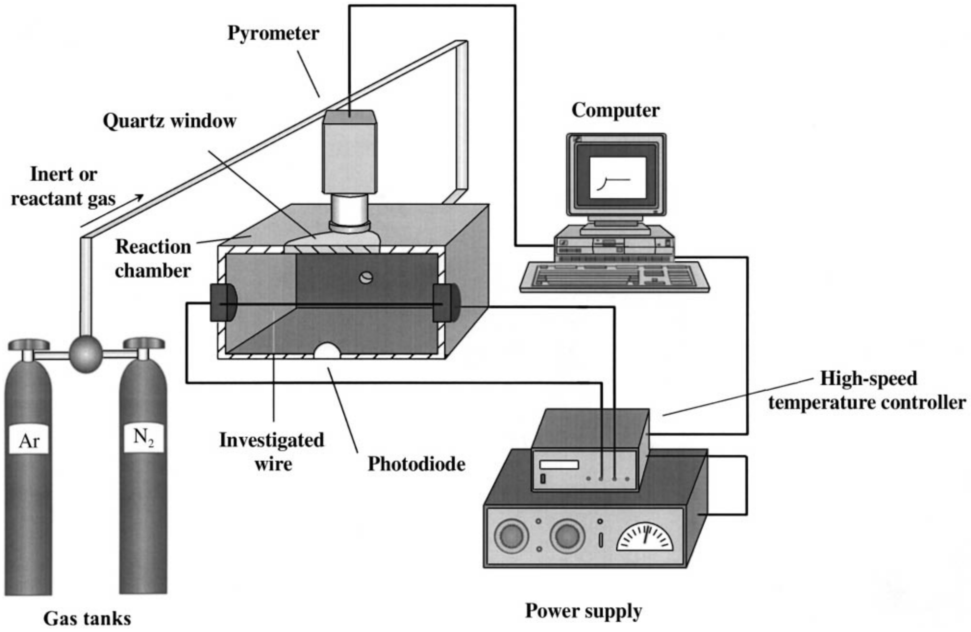

Fig. 1. Schematic diagram of the computer-assisted electrothermography set-up.

$T_m = 2070$ K higher than $T_{mp,\,Ti}$. To illustrate this effect, the dependence of T_m as a function of ω is shown in Fig. 3. In addition, if preheating rate exceeds a critical value, overshooting characteristics (T_m, duration) are also influenced by reference temperature, T_r. For example, at $\omega = 1.5 \times 10^5$ K/s, the duration of overshooting increases approximately two-fold by increasing T_r from 1840 to 1900 K (Fig. 2b).

As noted above, the CAE technique allows one to measure wire temperature, T as well as the voltage and current applied to the wire, leading to Joule heat, $p(t)$. The rate of chemical heat generation, $q(t)$, as a function of time, is given by the heat balance equation, which for a cylindrical geometry can be written as follows [5]:

$$\rho c_P \pi r_0^2 L \frac{dT}{dt} = q + p(t) - h(T) \quad (1)$$

where ρ is the density, c_P the heat capacity, r_0 the initial wire radius, L the wire length, $h(T)$ is the rate of heat loss.

In the regime of constant temperature, the method used to calculate kinetic parameters has been described elsewhere [6]. During overshooting, since the temperature is not constant, $dT/dt \neq 0$. However, $h(T)$ can still be defined by conducting experiments under conditions where the contribution from chemical reaction is negligible (e.g. when reaction is complete, or in inert atmosphere). Also, $p(t) = 0$

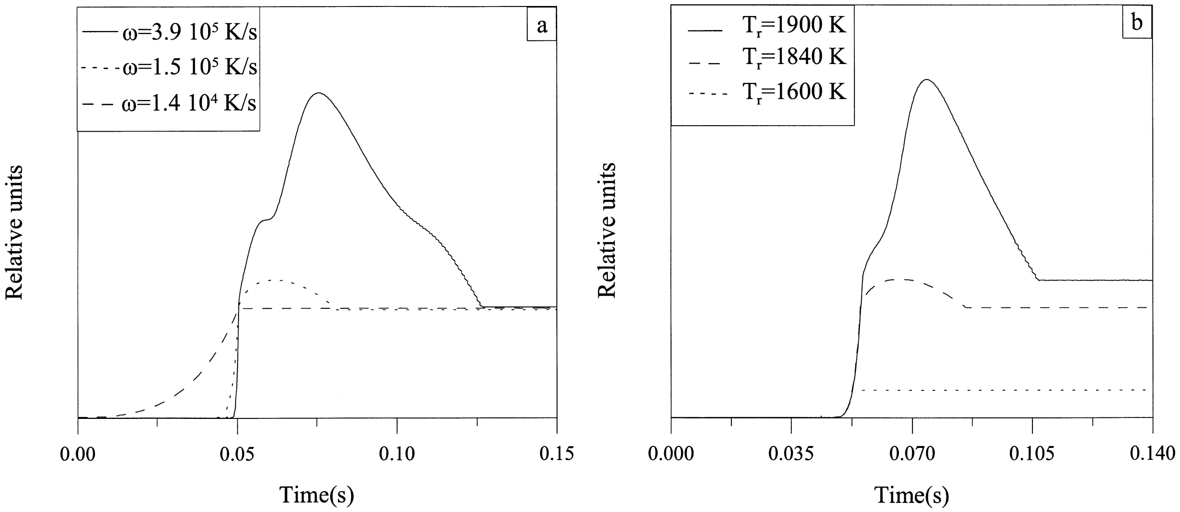

Fig. 2. Temperature–time profiles for Ti wires reacted with N$_2$ under (a) different preheating rates, $T_r = 1840$ K; (b) different setpoints, $\omega = 1.5 \times 10^5$ K/s.

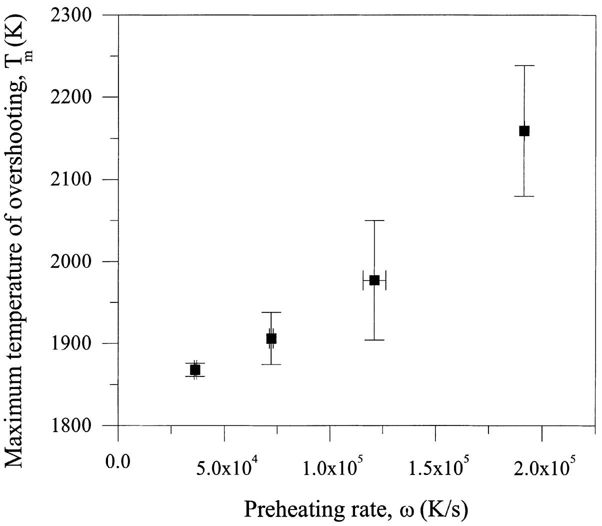

Fig. 3. Maximum temperature, T_m reached during overshooting as a function of preheating rate ω, $T_r = 1840\,K$.

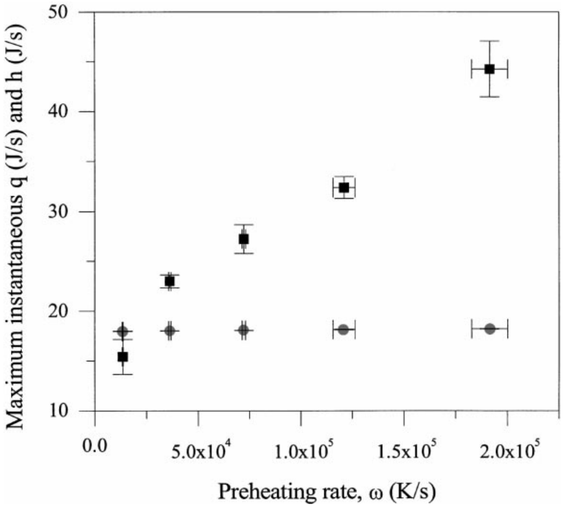

Fig. 4. Maximum instantaneous rate of heat generation, q reached during overshooting (■) and rate of heat loss, h (●) as functions of preheating rate, ω.

during overshooting. Thus, by calculating the instantaneous derivative of temperature, dT/dt, from the experimental $T = T(t)$ curves and by using Eq. (1), one may obtain $q(t)$ during this nonisothermal process. Finally, numerical integration of $q(t)$ leads to the cumulative heat generated by chemical reaction, $Q(t)$. Using this approach, the dependence of maximum rate of heat generation, q_m reached during the reaction as a function of preheating rate is shown in Fig. 4. It may be seen that q_m increases about three times when preheating rate changes in the range 1.4×10^4–2×10^5 K/s.

To obtain specific kinetic parameters from $Q(t)$, we utilize the sharp-interface model [10], with diffusion of nitrogen through the product layer being the rate-determining step, which was used successfully in our prior work for the constant temperature regime [5,6]. In this case, the position of the reaction interface, r_c (radius of the unreacted core) is obtained from $Q(t)$ by the relation:

$$r_c^2 = r_0^2 - \frac{Q(t)}{-\Delta H\,\rho\pi L} \tag{2}$$

where ΔH is the enthalpy of reaction.

Further, for this model, the governing equations and the corresponding boundary and initial conditions are

$$\frac{\partial c}{\partial t} = D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right); \qquad r_c < r < r_0 \tag{3}$$

$$c(r_0, t) = c_0, \qquad c(r_c, t) = 0 \tag{4}$$

$$\frac{dr_c}{dt} = -2\frac{D}{\rho}\left.\frac{\partial c}{\partial r}\right|_{r=r_c} \tag{5}$$

$$r_c(0) = r_0 \tag{6}$$

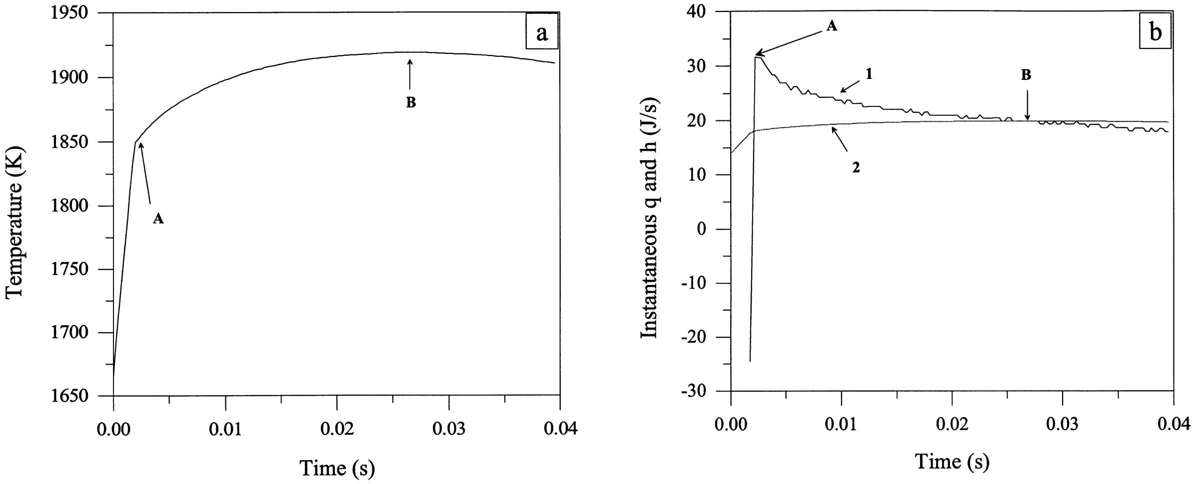

Fig. 5. (a) Temperature–time profile for Ti wire reacted in N_2 with $\omega = 1.5 \times 10^5$ K/s, at $T_r = 1840\,K$; (b) instantaneous rate of heat generation by chemical reaction, $q(1)$ and rate of heat loss, $h(2)$ as functions of time.

where c is the concentration of N_2 and D is its diffusion coefficient in the product layer, given by

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

Using the pseudo-steady-state approximation, solving Eqs. (3) and (4) yields

$$\frac{dc}{dr} = \frac{c_0}{r \ln(r_0/r_c)} \tag{8}$$

Substituting this in Eq. (5) and integrating gives:

$$r_0^2 - r_c^2 + r_c^2 \ln\left(\frac{r_c^2}{r_0^2}\right) = \frac{8c_0}{\rho}\int_0^t D[T(t)]\,dt \tag{9}$$

Knowing the value of r_c as a function of time (Eq. (2)) and using experimental temperature–time dependence (see Fig. 5a, for example), one may conduct a non-linear least-squares analysis to obtain the activation energy, E_a and pre-exponential factor, D_0 (cf. [11]). More specifically, if Y_m represents the left-hand side of Eq. (9) measured experimentally, one needs to find the values of E_a and D_0 that minimize the quantity $\sigma^2 = \sum_{i=1}^{N}(Y_{mi} - Y_{ci})^2/(N-2)$, where Y_{ci} is the calculated value using the right-hand side of Eq. (9), and N is the number of data points. Thus, by independently varying E_a and D_0, one can obtain the minimum value for σ^2. Using this approach, the best fitted values of E_a and D_0 were determined to be 330 kJ/mol and 4.8×10^{-2} m^2/s, respectively. Further, these values were essentially independent of the overshooting conditions.

4. Discussion

It was observed that under certain conditions, when preheating rate and reference temperature are above critical values, nitridation of the titanium wire under a steady flow of nitrogen cannot occur in constant temperature regime and an overshooting phenomenon takes place. It was also shown how preheating rate and reference temperature influence the characteristics of overshooting. Increasing either one leads to an increase in the duration, maximum temperature and, hence the rate of chemical reaction during overshooting.

4.1. Overshooting as an ignition phenomenon

To understand the nature of overshooting, let us compare typical time dependencies of the rate of heat generation by chemical reaction [$q(t)$], calculated by Eq. (1) (curve 1, Fig. 5b) and independently obtained rate of heat loss [$h(t)$] (curve 2, Fig. 5b). The latter is plotted taking into account observed temperature–time history of the process (see for example Fig. 5a). It can be seen that overshooting occurs when $q > h$. Note that in Fig. 5b, point A corresponds to the start of overshooting [$p(t) = 0$], while point B to the maximum temperature reached during overshooting (compare with Fig. 5a). These graphs clearly illustrate that the observed phenomenon can be considered as ignition of titanium wire–nitrogen system (cf. [12,13]). Indeed, the critical conditions of ignition, when the rate of chemical generation at a certain temperature becomes equal to the heat loss, are achieved at some point of the process temperature–time history. After this point, no additional heat is needed to maintain the reaction and temperature continues to rise. However, as reaction proceeds, the chemical generation rate decreases (parabolic law), while heat losses increase and at some point B, q becomes again equal to h, after which temperature starts to decrease.

It was also shown that for the investigated system, both in isothermal [6] and nonisothermal conditions (see Fig. 4), the rate of heat generation by chemical reaction strongly depends on preheating rate: higher preheating rates lead to higher values of q. Since the rate of heat loss is essentially independent of preheating rate (Fig. 4), it is clear that at some critical value of the latter, q becomes larger than h and, hence ignition occurs. This also explains why overshooting has more pronounced characteristics at higher preheating rates.

4.2. Isothermal and nonisothermal kinetics

Note that during overshooting, although temperature often exceeds the melting point of titanium, the wire does not break due to the outer layer of solid reaction product formed prior to the melting point. Due to this fact, by using the approach described above (see Results section), one can extract kinetic parameters based on data obtained during this essentially nonisothermal process.

In our previous work, the Ti–N_2 reaction kinetics were calculated in the isothermal regime [5,6]. It was found that the preheating rate does not influence the activation energy, and that the obtained value of $E_a = 210 \pm 25$ kJ/mol was in good agreement with values reported in the literature for diffusion of N_2 in TiN [7–9]. The value of E_a obtained in this study, based on treatment of nonisothermal data during overshooting ($E_a = 330$ kJ/mol) is significantly higher. Note, however, that this value is in good agreement with a previous value reported in the literature (342 kJ/mol) essentially obtained under nonisothermal conditions of a combustion wave [14]. This behavior may have two possible explanations: either reaction in the overshooting mode is more activated as compared to isothermal conditions, or the sharp-interface model used to analyze the data is not valid in the nonisothermal case. Regardless of the true reason, the conclusion can be reached that kinetics obtained under isothermal conditions may in general not be applicable under nonisothermal ones.

4.3. Influence of heat treatment on metal reactivity

In order to shed further light on the effect of preheating conditions on the overshooting phenomenon, additional

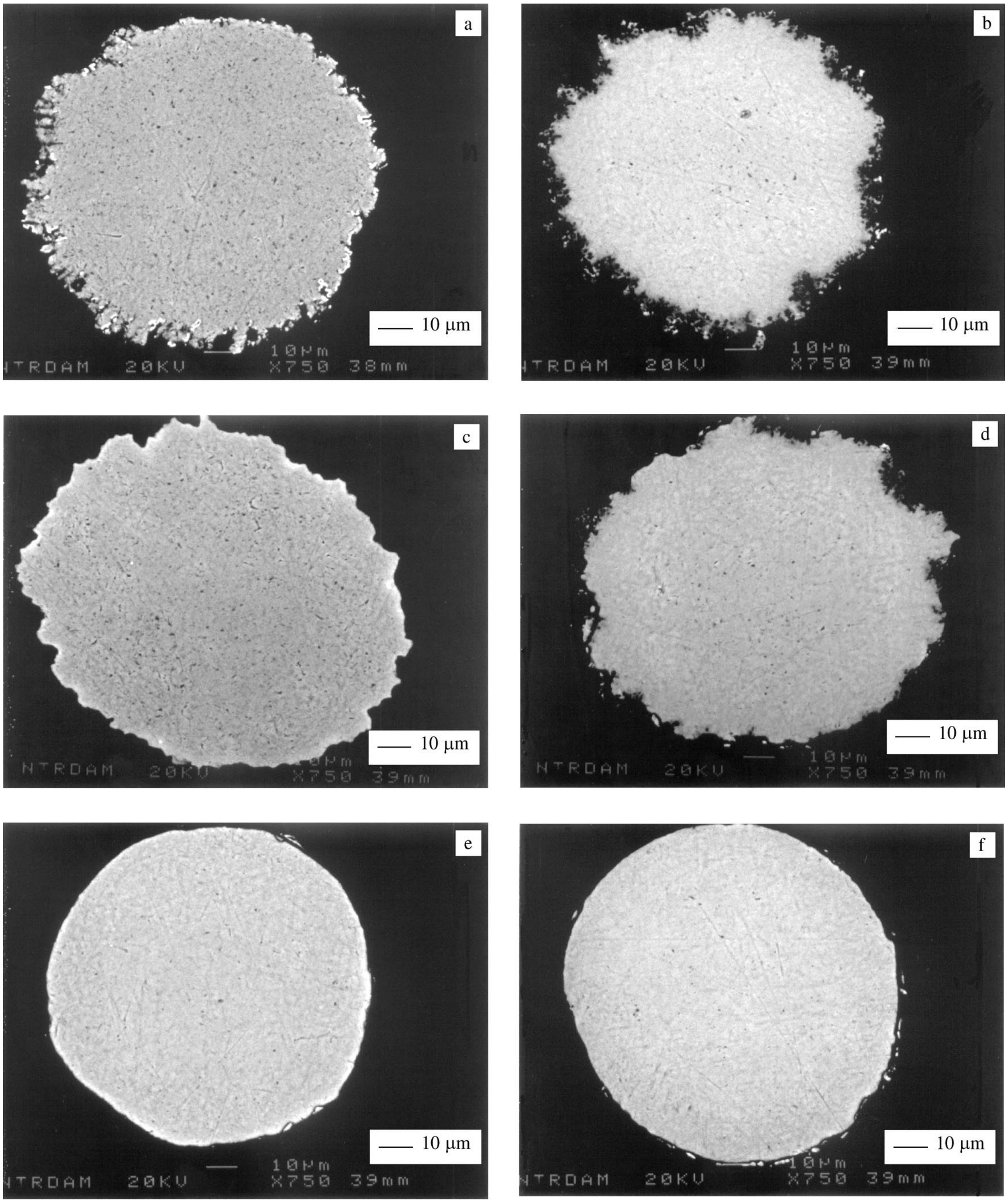

Fig. 6. Typical cross-sections of Ti wires treated under different conditions: (a) initial; (b) reacted in N_2 at $T_r = 1840\,K$, $\omega = 3.4 \times 10^5$ K/s; (c) treated in Ar for 0.1 s at $T_r = 1360\,K$, $\omega = 1.2 \times 10^4$ K/s; (d) pretreated in Ar for 0.1 s ($T_r = 1360\,K$, $\omega = 1.2 \times 10^4$ K/s), and then reacted in N_2 at $T_r = 1840\,K$, $\omega = 3.4 \times 10^5$ K/s; (e) treated in Ar for 10 s at $T_r = 1730\,K$, $\omega = 1.2 \times 10^4$ K/s; (f) pretreated in Ar for 10 s ($T_r = 1730\,K$, $\omega = 1.2 \times 10^4$ K/s), and then reacted in N_2 at $T_r = 1840\,K$, $\omega = 3.4 \times 10^5$ K/s.

studies were conducted. The characteristic microstructures of initial Ti wire and after overshooting are shown in Fig. 6a and b, respectively. It can be seen that both wires have irregular surfaces with relatively high surface area and that these irregularities increase further after overshooting, probably due to the fact the wire temperature exceeded $T_{\mathrm{mp,\,Ti}}$ in this specific case.

Special model experiments were conducted to investigate the influence of heat treatment alone on the microstructure of metal reactant. For this, titanium wires were pretreated in inert gas atmosphere (ultra high purity argon) under different temperature–time schedules. It was shown that in general, such annealing leads to smoothening of the wire surface (i.e. decrease in specific surface area). For example, heating

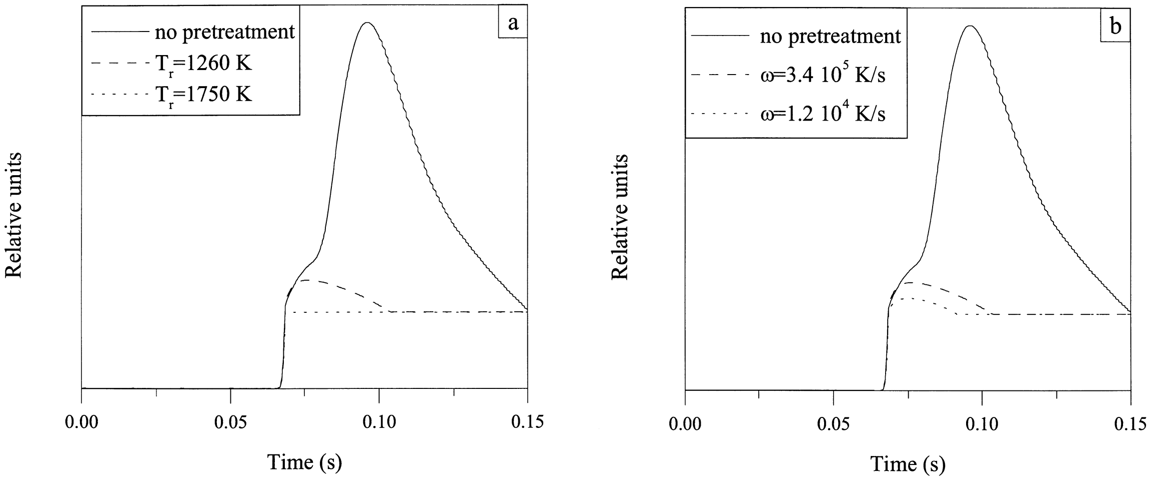

Fig. 7. Influence of pretreatment conditions in Ar during 0.1 s on overshooting characteristics ($T_r = 1840$ K, $\omega = 3.4 \times 10^5$ K/s): (a) effect of T_r, $\omega = 3.4 \times 10^5$ K/s; (b) effect of ω, $T_r = 1260$ K.

in Ar for 0.1 s at relatively low T_r and ω leads to minor microstructural changes (Fig. 6c) as compared to the initial wire. However, wires treated for 10 s at higher temperatures become perfectly smooth (Fig. 6e).

Even more interesting is that a change in the wire microstructure affects the overshooting parameters (T_m, q_m, duration, etc.). One may compare the microstructures of different wires after reaction in nitrogen under conditions where overshooting was detected for non-annealed wires. For the wire treated in Ar for 10 s at high T_r (1730 K), no overshooting was detected and the surface of the final sample did not change significantly during reaction in N_2, remaining smooth (compare Fig. 6e and f). Some intermediate structures and overshooting features were observed for samples annealed for shorter periods of time (Fig. 6c and d).

In more details, it was observed that changing the reference temperature during the annealing of wires in inert atmosphere affected the extent of overshooting. The wires pretreated in Ar for the same duration (0.1 s) and preheating rate (e.g. 3.4×10^5 K/s), but different T_r, were then reacted in N_2 under conditions of high overshooting (high ω and T_r). As shown in Fig. 7a, it is remarkable that the wire annealed at 1750 K even for 0.1 s, exhibits no overshooting. Similarly, when T_r during pretreatment in inert gas was kept constant, but ω was changed, it was observed that wires annealed at lower preheating rates and then reacted in N_2 showed lower overshooting features (Fig. 7b). However, even with a high preheating rate (3.4×10^5 K/s) during annealing in Ar, the overshooting in N_2 is not as high as compared to the non-annealed samples.

Thus, on one hand, decrease in preheating rate leads to a decrease in the rate of chemical reaction in the Ti–N_2 system, when reaction occurs in overshooting mode (Fig. 2a). On the other hand, decreasing the solid reactant specific surface area (e.g. by annealing in Ar) leads to the same effect. Moreover, pretreatments in Ar at higher T_r and lower ω lead to more pronounced reaction slowdown. All above support the hypothesis developed in our previous work [6] that lower preheating rates to the setpoint reaction temperature provide more change in the metal reactant microstructure (primarily reduction of specific surface area), which decreases the rate of subsequent chemical interaction. Contrarily, high preheating rates do not modify the metal surface, which then maintains high rate of chemical reaction.

Acknowledgements

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