Influence of Preheating Rate on Kinetics of High-Temperature Gas–Solid Reactions

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The influence of preheating rate on kinetics of high-temperature reactions in gas – solid systems was investigated by a computer-assisted electrothermography technique. Two systems were investigated: $Nb-N_2$ and $Ti-N_2$, in the temperature ranges 2,100 – 2,500 K and 1,350 – 1,600 K, respectively. The results showed that for both systems, reaction kinetics are enhanced by increasing the preheating rate to the desired reaction temperature. Analysis of the experimental data in the context of the sharp-interface model showed that the activation energy of the diffusion coefficient does not depend on heating rate, while the preexponential factor is affected. Additional experiments suggest that nonisothermal preheating, even though of short duration, about 10 ms, influences chemical reactivity of the solid reactant by changing its specific surface area.

Introduction

A variety of processes involving chemical reactions occur under nonisothermal conditions, where temperature changes with time. In these cases, the following fundamental questions arise. How does heating rate influence the rate of chemical reaction? Can one use kinetic data obtained under isothermal conditions to describe the essentially nonisothermal processes? If not, how can nonisothermal kinetics be measured?

These issues become important when characteristic heating rate of the process reaches the range 10^3-10^6 K/s. Such extreme conditions occur, for example, in heterogeneous combustion wave during synthesis of advanced materials (cf. Varma et al., 1998). This combustion synthesis (CS) process is based on the concept that once initiated locally, a highly exothermic wave of chemical interaction self-propagates rapidly through the reaction medium and is characterized by extremely fast heating rates (up to 10^6 K/s), high temperatures (up to 3,500 K), and short reaction times (on the order of seconds). Some results available in the literature show that heating rate may influence phase formation and chemical interaction in such processes (cf. Philpot et al., 1987; Deevi, 1992; Kharatyan and Chatilyan, 1999). However, no detailed kinetic investigations have been reported in this direction.

We have developed a computer-assisted electrothermography method (CAE) to determine the intrinsic kinetics of reactions under conditions similar to those realized during CS (Pelekh et al., 2000). Some preliminary results obtained for the interaction in the titanium–nitrogen system show that the reaction rate depends on the preheating rate of the reaction system (Pelekh et al., 1999). In the present work, by using the CAE method, the detailed kinetics of chemical reaction in the niobium–nitrogen and titanium–nitrogen systems were investigated in the range of preheating rates $10^4-5\times10^5$ K/s. It was quantitatively shown that high preheating rates lead to an increase of reaction rate in both systems. An explanation of the observed phenomenon, based on heating rate influence on the specific surface area of solid reactant, is suggested.

Experimental Technique and Procedures

A CAE setup (see Figure 1), designed and built in our laboratory specifically to investigate the influence of preheating rate on the reaction behavior, is described elsewhere (Pelekh et al., 2000). Briefly, for gas–solid systems, a metal wire (such as Nb or Ti) is placed in a reaction chamber under a steady flow of gaseous reactant (such as nitrogen). The wire is heated uniformly to the desired temperature (T_r) by applying electric current. The temperature is measured by a photodiode, which is calibrated using a two-color pyrometer (Ircon MR-OR10-99C). A specially designed high-speed temperature controller allows us to change preheating rate in in the range $10^4-5\times10^5$ K/s as well as to keep T_r constant (so-called constant

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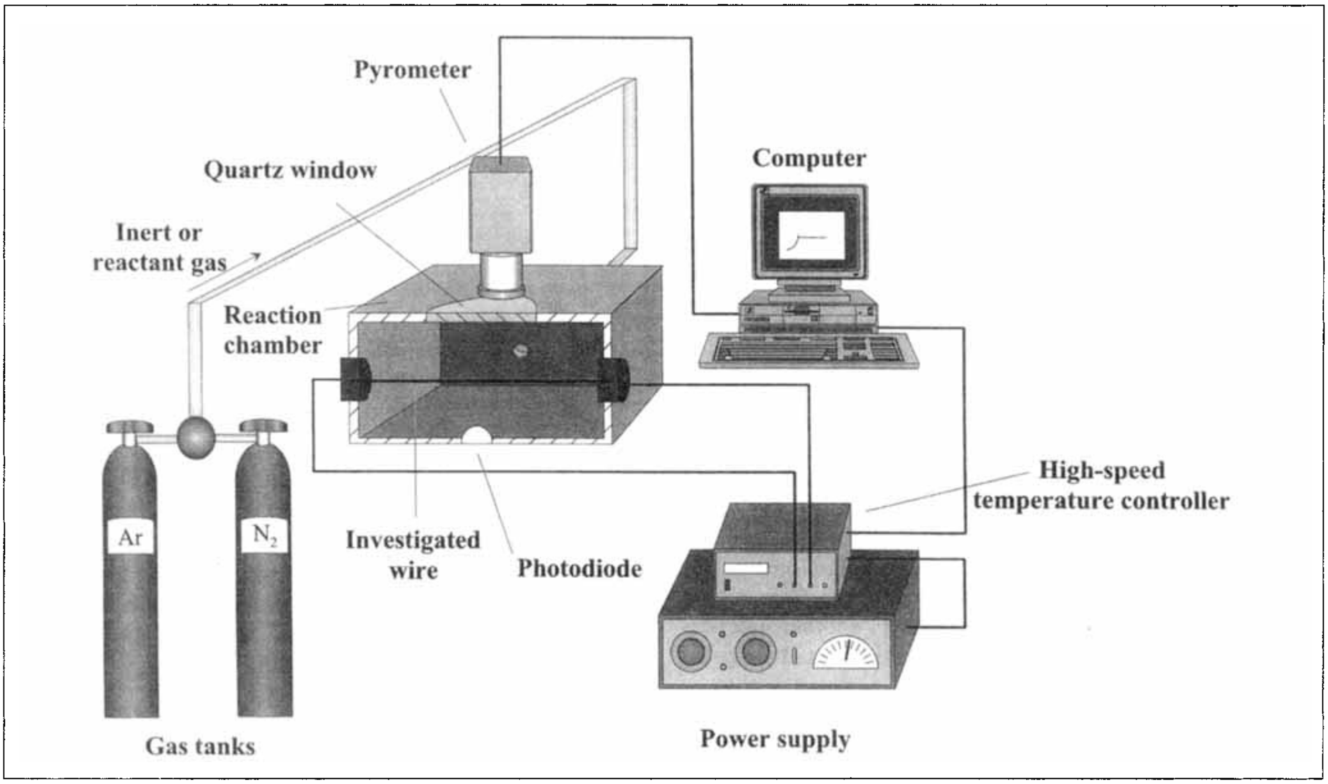

Figure 1. Computer-assisted electrothermography setup.

temperature regime). More specifically, the signal of the photodiode is amplified and compared with a preset reference voltage corresponding to the desired temperature. If the former is higher (lower), meaning that the wire temperature is greater (smaller) than T_r, then the voltage applied to the wire decreases (increases), leading to a temperature reduction (increase). A computer equipped with a data-acquisition board (Data Translation, DT2821) collects the experimental data, including Joule heat, $p(t)$, generated in the wire.

The rate of chemical heat generation, $q(t)$, as a function of time, is given by the heat-balance equation, which for a cylindrical wire can be written as follows (cf. Pelekh et al., 1999):

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

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

In the regime of constant temperature, since $q(t)$ varies with time as the reaction proceeds, the controller varies the electric power $p(t)$ by using the feedback loop described earlier. Under these conditions ($dT/dt = 0$) from Eq. 1, and we

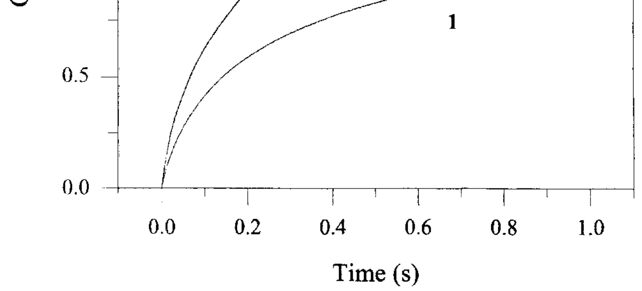

Figure 2. For niobium wires reacted in nitrogen, cumulative heat generated, Q, as a function of time for T_r = 2,500 K and different preheating rates: 1-3 × 10^4 K/s: 2-2 × 10^5 K/s.

Table 1. Experimental Data for Cumulative Heat Generated, Q at t = 1 s, as a Function of Reaction Temperature, T_r, and Preheating Rate

	Q, J	
T_r, K	~ 3 × 10^4 K/s	~ 2 × 10^5 K/s
2,090	0.25	0.34
2,215	0.50	0.65
2,310	0.71	0.89
2,415	1.08	1.38
2,500	1.11	1.75

have

$$q(t)|_T = h(T) - p(t)|_T. \tag{2}$$

Further, $h(T)$ can be defined by conducting measurements under conditions where the contribution from the chemical reaction is negligible (such as when the reaction is complete, or in inert atmosphere). In this case, $q = 0$, and from Eq. 2, we have $h(T) = p(T)$. Further, knowing $h(T)$, we can retrieve $q(t)$ from the recorded $p(t)$. Finally, the cumulative heat generated by the chemical reaction, $Q(t) = \int_0^t q(t)dt$, can be readily calculated.

Thus, by conducting experiments at various temperatures, and measuring $p(t)$, one can obtain the temperature-time dependence of the cumulative heat-generation function, $Q(t)$. Then, by mathematical treatment of the obtained data (cf. Pelekh et al., 1999 for details), and assuming a specific model of gas-solid interaction, one can define the kinetic law and extract the kinetic parameters (such as activation energy, E_a; reaction order) of the investigated chemical reaction.

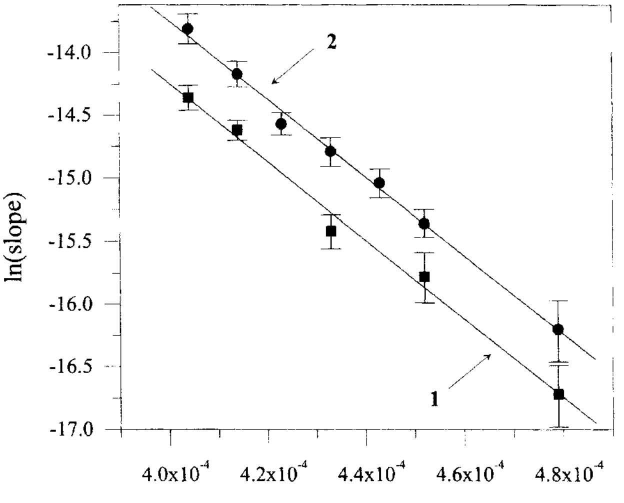

Figure 4. Temperature dependence of the slope of Eq. 3 in Arrhenius coordinates for the Nb–N_2 system, for two different preheating rates: 1–3 × 10^4 K/s; 2–2 × 10^5 K/s.

In the present work, in addition to CAE, another independent approach was used to extract kinetic data. It appears that in the regime of constant temperature, turning off the electric power leads to rapid (~ 10^4 K/s) cooling of the wire and hence quenching of the reaction process. Thus, by switching off the power at different stages of interaction, followed by microstructural investigation of the quenched samples, one can also obtain information about the reaction kinetics (cf. Vadchenko and Grigor'yev, 1975). In our case, the microstructures, phase, and elemental compositions of cross sections and surfaces of quenched wires were determined by different methods including scanning electron microscopy (JSM 6400, JEOL), X-ray diffraction (X1 Advanced Diffrac-

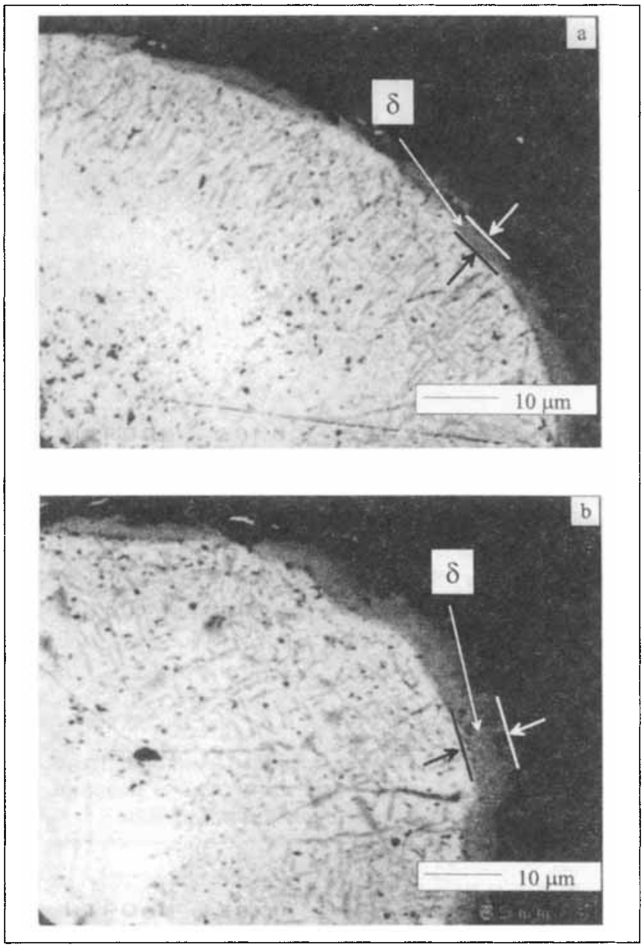

Figure 3. Typical cross sections of Nb wires reacted in nitrogen at 2,500 K for 0.2 s with different preheating rates: (a) 3 × 10^4 K/s, (b) 2 × 10^5 K/s.

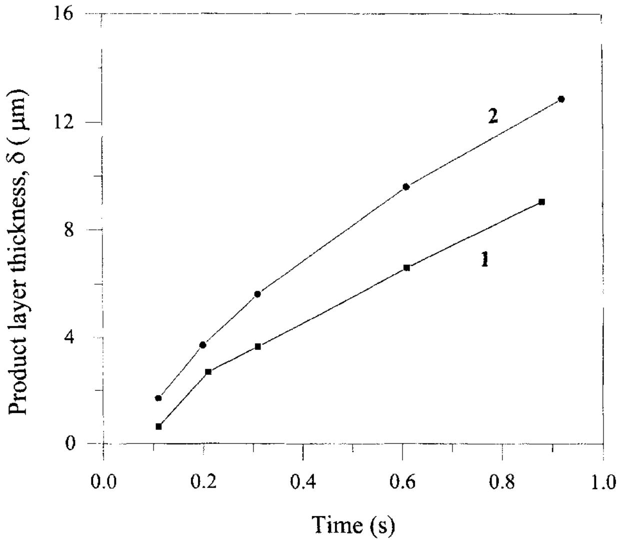

Figure 5. Typical kinetics of product layer growth for the Nb–N_2 system at T_r = 2,500 K: 1–3 × 10^4 K/s; 2–1.5 × 10^5 K/s.

tion System, Scintag Inc.), and energy dispersive X-ray microanalysis (SIGMA, Kevex).

The influence of heating rate on reaction kinetics in two gas–solid systems, that is, Nb–N_2 and Ti–N_2, was investigated. Metal wires (100-μm diameter) of niobium and titanium (both from Electronic Space Products International) were treated in flowing oxygen-free nitrogen (< 0.5 ppm O_2). For the Nb–N_2 system, the temperature was varied from 2,100 K to 2,500 K while for titanium, the temperature range was 1,350–1,600 K. These temperature values are below the melting points of metal reactants ($T_{mp,\mathrm{Nb}}$ = 2,741 K; $T_{mp,\mathrm{Ti}}$ = 1,948 K), and in the range encountered during combustion synthesis.

Results

Nb – N_2 system

A plot of the cumulative heat generated, $Q(t)$, as a function of time for a reference temperature, T_r = 2,500 K, and two different heating rates is shown in Figure 2. As can be seen, for the entire duration of the experiment, Q is higher when the wire is preheated at the higher rate. This behavior was observed for all T_r values (2,100–2,500 K), and the calculated Q values at t = 1 s for several T_r are shown in Table 1. This clearly shows that the preheating rate significantly influences reaction kinetics.

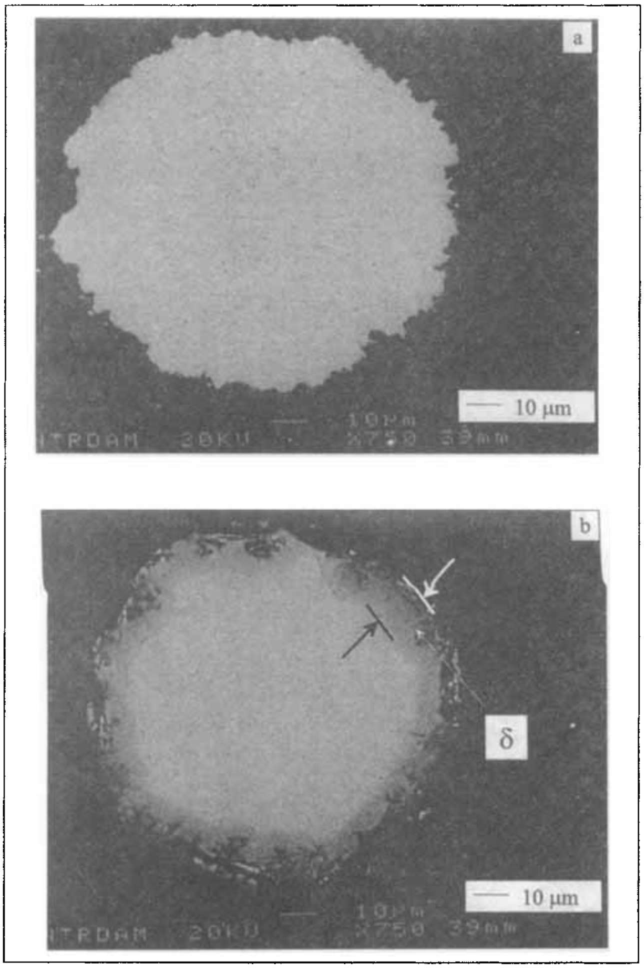

Figure 6. Typical cross sections of Ti wires reacted in nitrogen at T_r = 1,700 K, with preheating rate ~ 1.2 × 10^4 K/s for (a) ~ 1 s; (b) ~ 10 s.

Characteristic cross sections (backscattering image) of quenched Nb wires after short-term (0.2-s) heat treatment in nitrogen at T_r = 2,500 K are shown in Figure 3. As may be seen, the microstructures are characterized by the existence of two regions: a thin product layer (thickness δ) with relatively lower average atomic number (dark phase) and the core, in which the lesser amount of nitrogen is dissolved (light phase). This qualitative observation was confirmed by EDX microanalysis, which showed that an average amount of nitrogen in the core is less than 1 mass %, while in the surface film, it is between 4 and 6 mass %. For this reason, the sharp-interface model (cf. Doraiswamy and Sharma, 1984) can be considered to describe the progress of the reaction in the investigated system.

It is known (see Pelekh et al., 1999, for details) that in this case, a parabolic-type law holds and radius of the unreacted core, r_c, changes with time as follows:

$$r_0^2 - r_c^2 + r_c^2 \ln\left(\frac{r_c^2}{r_0^2}\right) = \frac{8Dc_0}{\rho}t, \qquad (3)$$

where D is the diffusion coefficient of the reactant gas in the product layer, which varies with temperature as $D_0 \exp(-E_a/RT)$; E_a is the activation energy; and c_0 is the concentration of reactant gas at $r = r_0$. Then, a plot of the function $[(r_0^2 - r_c^2) + r_c^2 \ln(r_c^2/r_0^2)]$ vs. t should give a straight line, with slope proportional to the diffusion coefficient, D.

On the other hand, a relationship exists between r_c and cumulative heat generated by the chemical reaction, as fol-

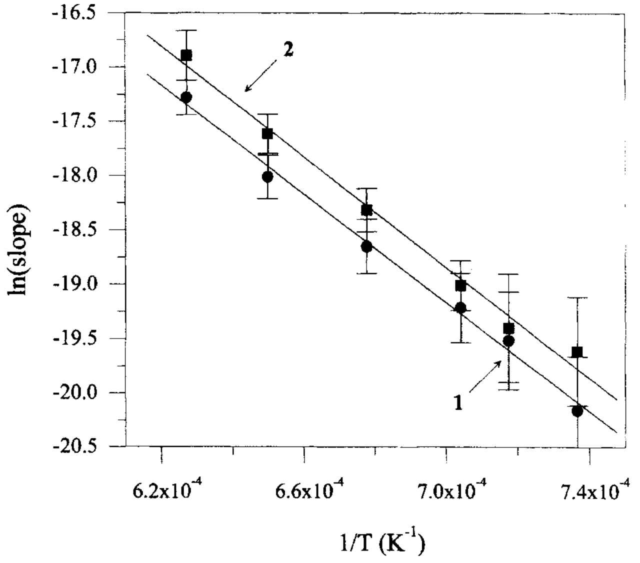

Figure 7. Temperature dependence of the slope of Eq. 3 in Arrhenius coordinates for the Ti–N_2 system, for two different preheating rates: 1–1.2 × 10^4 K/s; 2–1.6 × 10^5 K/s.

lows:

$$r_c^2 = r_0^2 - \frac{Q(t)}{(-\Delta H \rho \pi L)}, \qquad (4)$$

where ΔH is the enthalpy of reaction ($Nb + 1/2N_2 \rightarrow NbN$, $\Delta H = -230$ kJ/mol). Thus, conducting experiments at different temperatures, one can convert experimental results [that is, $Q(t)$] into $r_c(t)$ following Eq. 4 and plot the slope of the function defined by Eq. 3 in Arrhenius coordinates. If the sharp-interface model is valid, then a straight line should be obtained.

Examples of such dependencies for two different heating rates are presented in Figure 4. Each data point represents average of at least ten different wire samples. First, it can be seen that the lines are essentially straight, so that the sharp-interface model describes the reaction in the $Nb-N_2$ system well, over the entire range of temperatures. Second, within experimental accuracy, slopes of the curves obtained for different heating rates are the same. Thus activation energy of diffusion, E_a, and the reaction mechanism do not depend on heating rate, at least over the investigated range. The average value of E_a is equal to 260 kJ/mol. Note that widely varying values for the $Nb-N_2$ system have been reported in the literature, ranging from 150 kJ/mol to 320 kJ/mol (cf. Ang, 1953; Boratto and Reed-Hill, 1977; Musenich et al., 1994) so that a definitive comparison cannot be made.

However, it is apparent that the absolute values of rates are smaller for samples preheated to T_r with lower heating rates (compare lines 1 and 2, Figure 4) for the entire range of investigated temperatures. Following Eq. 3, this means that the preexponential factor in the kinetic law, which involves D_0 and c_0, depends on the heating rate and decreases with decreasing rate of preheating metal reactant to the desired temperature.

Further, detailed statistical analysis of wire microstructures (each data point represents the average of at least 80 measurements, taken on four different wire cross sections) was conducted to verify this conclusion. For this, the wires were heated to different temperatures and then "quenched" after different times of isothermal heat treatment. For example, the dependence of δ as a function of time for different heating rates and $T_r = 2,500$ K is shown in Figure 5. It can be seen that thickness of product layer after preheating at higher heating rate is larger (see also Figure 3a and 3b). Moreover, this difference increases with increasing time of heat treatment.

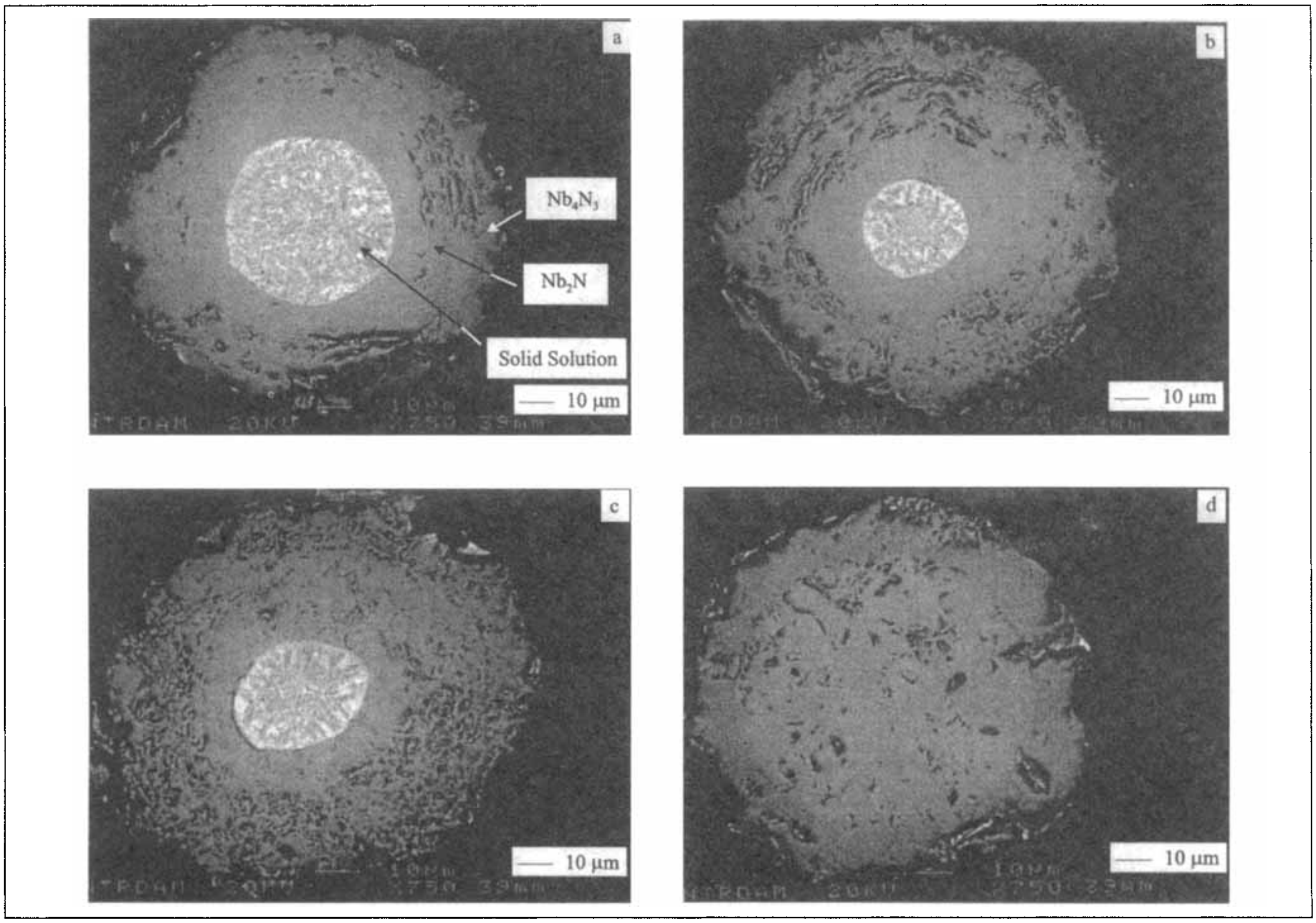

Figure 8. Typical cross sections of Nb wires reacted in nitrogen at $T_r = 2,500$ K for 3 s (a,b) and 5 s (c,d) with different preheating rates: (a,c) 3×10^4 K/s: (b,d) 2×10^5 K/s.

Ti–N_2 System

Due to the previously described overshooting phenomenon (Pelekh et al., 1999), a range of relatively low temperatures (1,350–1,600 K) was used to investigate the kinetics of interaction in the Ti–N_2 system, in the regime of constant temperature. Primarily owing to the lower temperatures, even after 1s of treatment in nitrogen, it was impossible to detect by SEM the product layer on the surface of quenched titanium wires (Figure 6a). However, XRD analysis conducted on such wires clearly showed that the TiN phase was present as the main formed product during the treatment. Taking into account that this phase was clearly detected by EDX in the product layer, δ, after 10 s of treatment (Figure 6b), one can conclude that the sharp-interface model is again suitable to describe reaction in the Ti–N_2 system.

The characteristic Arrhenius plots for the titanium-nitrogen reaction obtained by using the approach described earlier are presented in Figure 7. In general, the results are similar to those observed for the Nb–N_2 system. Since the slopes of lines obtained for different preheating rates are the same, the activation energy does not depend on heating rate. The obtained $E_a = \sim 210$ kJ/mol is close to values reported in the literature for diffusion of N_2 in TiN (cf. Wasilewski and Kehl, 1954; Bars et al., 1977; Antilla et al., 1983; Pelekh et al., 1999). However, higher rates of preheating again lead to faster reactions at the same reference temperature.

Discussion

It is shown clearly earlier that the preheating rate influences the kinetics of reactions in the Nb–N_2 and Ti–N_2 systems. In the framework of used model, this effect is explained by the change of the preexponential factor, while E_a remains constant. This factor contains both diffusion coefficient (D_0) and characteristic concentration (c_0) of the reacting gas (see Eq. 3). In order to shed further light on the observed effect, additional sets of experiments were conducted.

First, several niobium wires were treated in nitrogen for 0.1 s under the same heating conditions (preheating rate and reference temperature), so that essentially identical initial product layer formed on the surface of all wires. Then, these wires were further reacted in nitrogen for 0.2 s at temperature T_r; however, they reached T_r with different heating rates. The results of these experiments consistently showed that the product layer continues to grow faster in the case of wires heated with higher rates (such as 2.7 μm with 2×10^5 K/s, against 1.7 μm with 3×10^4 K/s). This suggests that differences in reaction rates are not due to c_0.

Second, up to now, we considered relatively short reaction times (less than 1 s), when it can be expected that the system has memory of the thermal prehistory. It is interesting to determine the duration for which the reaction rate continues to be affected by the initial heating rate. For this, we compared the thickness of product layers formed on quenched wires that reacted in nitrogen during the longer times (1 to 10 s) at the same temperature, but were preheated to this temperature with different heating rates. In this context, note that preheating period is typically 10–50 ms, while thermal relaxation time is less than 1 ms. Typical cross sections of reacted wires quenched at different times are shown in Figure 8. Clearly, after a longer reaction period, three phases (two layers and the core) can be distinguished, namely, solid solution, Nb_2N, and Nb_4N_3. It is evident that the characteristic thickness of the Nb_xN product layers formed after the high preheating rate are larger as compared to samples preheated at lower rates. In fact, the Nb_2N phase reached the wire center in 5 s for preheating rate 2×10^5 K/s (Figure 8d), while a distinct region of solid solution is visible at rate 3×10^4 K/s

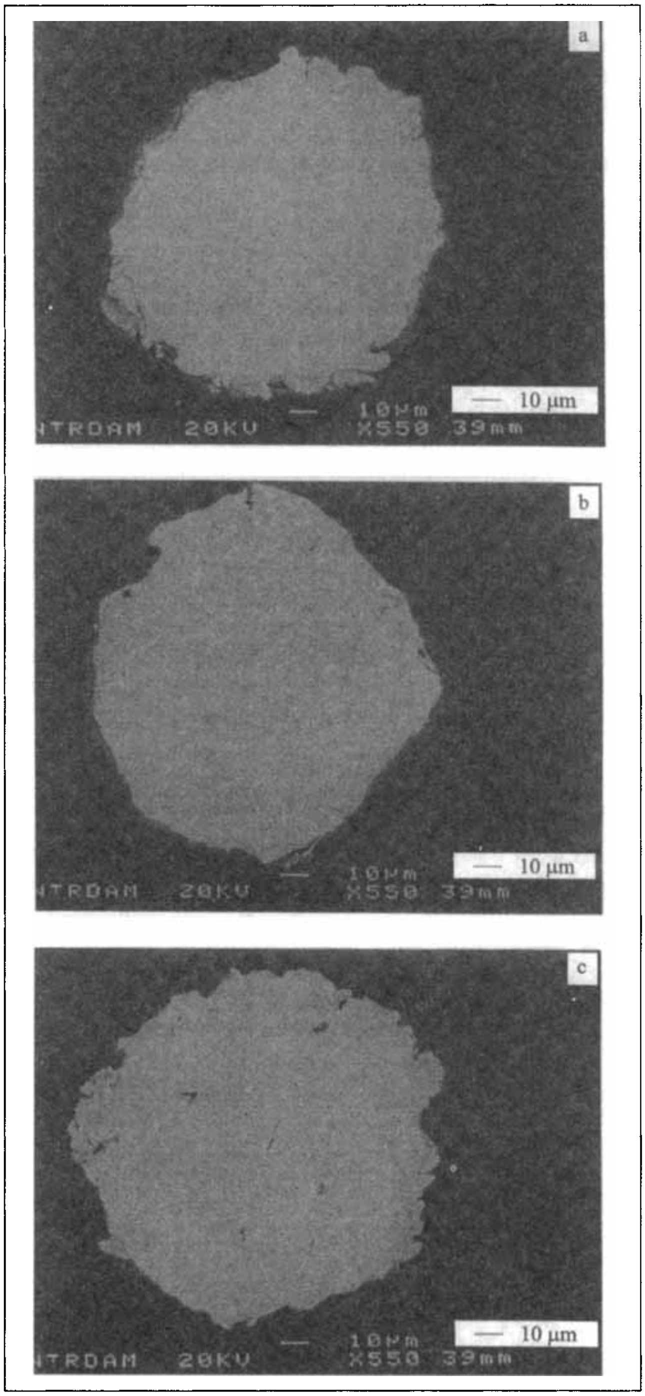

Figure 9. Typical cross sections of initial Nb wire (a) and wires treated in Ar for 0.1 s with different preheating rates: (b) 3.3×10^4 K/s; (c) 2.3×10^5 K/s.

(Figure 8c). The results of these experiments suggest that short-term nonisothermal treatment causes permanent change in intrinsic reactivity of the solid reactant, influencing D_0.

In order to verify this hypothesis, additional model experiments were conducted. The niobium wires were heat treated for 0.1 s in inert gas (high-purity argon) at the same reference temperature, T_r, but with different heating rates. Characteristic cross-sections of the various wires are shown in Figure 9. It can be seen that the surface of the wire treated with the lower heating rate (3.3×10^4 K/s) becomes smoother (surface area decreased; Figure 9b) as compared to the initial wire (Figure 9a). However, for the wire treated with higher heating rate (2.3×10^5 K/s), the surface area does not decrease, indeed formation of new defects (cracks, irregularities, etc.) can be observed (Figure 9c). This confirms the preceding hypothesis that even very short-duration (10–50 ms) heat treatment during preheating, when temperature increases up to the reference point, changes the reactivity of the solid reactant by affecting a specific surface area, that in turn significantly affects the rate of the subsequent chemical reaction.

Concluding Remarks

Based on independent measurements using computer-assisted electrothermography, it is demonstrated clearly that kinetics of gas–solid reactions, such as the $Nb-N_2$ and $Ti-N_2$ systems, are significantly influenced by the preheating rate used to reach the reference temperature. Analysis of the experiments suggests that the process of heating alters reactivity of the solid reactant, which leads to changes in the reaction kinetics. Further research on detailed characterization of the solid reactant surface as a function of heat treatment conditions is required to clarify the nature of the observed phenomena.

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