

STRUCTURE FORMATION MECHANISMS OF TITANIUM INFLAMMATION IN A NITROGEN ATMOSPHERE

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UDC 546

Experimental results on the structure- and phase-formation dynamics in rapid pulse heating of titanium powder in a nitrogen atmosphere are presented. A relation between the main macrokinetic ignition parameters and the microstructure formation process in the system studied is found.

The microstructure of different SHS (self-propagating high-temperature synthesis) materials and powders strongly depends on the concrete process performance [1]. In turn, the physical and chemical production mechanisms can be inferred from the characteristic structure and morphology of the combustion products. Therefore, studies of specific features of structure formation allow the combustion process to be investigated more thoroughly as a single physical effect and reveal feasibilities of producing a required final product with given characteristics.

At present, quite a number of publications on titanium nitride combustion and the SHS phase formation mechanism are known [2-8]. In pioneer Soviet studies [2-4] the conclusion was made that depending on the synthesis parameters in the titanium-nitrogen system two combustion operation modes (solid and liquid phase) could take place. The first is realized at low nitrogen pressures due to low (in comparison with metal melting temperature) real process temperatures [2]. At high gas pressures (>0.5 MPa) the second operation mode is realized and development of a nitrogen solid solution in liquid titanium is a leading process [3, 4].

In American studies [6-8] titanium combustion in a nitrogen atmosphere at low gas pressures (0.1 MPa) is considered. It is found that in such conditions thin nitride films and a nitrogen solid solution in β -titanium are "primarily" formed at the combustion front.

The high temperatures of the process ($T = 2500-2000$ K) and the short lifetimes of the "primary" structures in the combustion wave ($t \sim 0.01-0.5$ sec) make an experimental investigation of their development in dynamics very difficult. Absence of any data on the characteristic parameters of different "hardenings" [8] of these intermediate phases, used in all the above-mentioned publications, adds to the complexity of the problem.

In these circumstances new approaches to the study of the characteristic features of metal-gas interaction in the SHS wave have to be sought. In our opinion one of these approaches is investigation of processes with rapid ($U > 10$ K/sec) pulse heating of a titanium specimen in a nitrogen atmosphere. Detection of relations between the macrokinetic ignition parameters and the structure formation processes in a given system is of interest too.

1. Experimental Method. The titanium powder used (-100 mesh, ASTM) had a specific surface area $S = 0.2$ m²/g, average particle size $d = 70$ μ m, and main impurities (upper limit, mass %): Fe = 0.1; Si = 0.03; Ni = 0.06; C = 0.04; O = 0.89. The powder was compacted into specimens with a radius $r = 6$ mm and height $h = 15$ mm in the porosity range $\theta = 0.7-0.35$ relative unit. The PGS nitrogen used had the following impurity composition (vol. %): CO = 0.0002; CO₂ = 0.00030; CH₄ = 0.0005.

The specimens were placed in a reactor providing for: a) pre-evacuation up to $P = 10^{-3}$ MPa; b) blowing and filling with nitrogen up to $P = 1.5$ MPa; c) programmed heating of a specimen with an electric graphite up to $T = 2500$ K; d) pyrometer and thermocouple temperature measurement on the specimen surface and at its center (thermocouples: W-Re, 100 μ m; electronic pyrometer time constant of operation $\sim 10^{-4}$ sec).

As a rule, the specimens were heated by pulse heating: heating with a certain averaged heating rate U up to the temperature T_h with subsequent instant disconnection of the external power supply (Fig. 1a). The pressure of the nitro-

Institute for Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 64, No. 2, pp. 186-194, February, 1993. Original article submitted January 27, 1992.

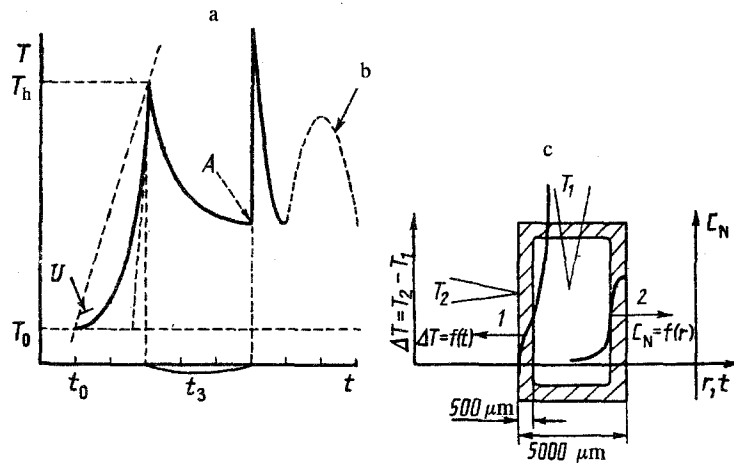


Fig. 1. Characteristic parameters of heating (a) (temperature T_h , K; heating rate U , K/sec; time t , sec) and inflammation (b) (ignition delay time t_d , sec); temperature difference ΔT (curve 1) at the surface (T_2) and in the center (T_1); specimen cross-sectional (r , μm) distribution of nitrogen concentration C_N , mass. % (curve 2).

gen atmosphere in which heat treatment of specimens was conducted was varied over the range $P = 5 \cdot 10^{-2}$ -1 MPa. The inflammation moment was determined by the specimen surface temperature discontinuity (point A in Fig. 1a).

In some experiments the gaseous reagent was "quickly" removed by nitrogen evacuation from the reactor at different time moments – before inflammation for hardening the structure – and phase-formation processes and their following investigation with scanning electron microscopy (SEM), x-ray phase (RPA) and local x-ray spectrum (LRSA) analyzes. The characteristic time for which the nitrogen pressure in the reactor fell from 1 to 10^{-3} MPa was ~ 0.5 sec. In view of the relatively low specimen heating temperatures ($T < 1700$ K), the information on the phase composition and particle morphology variation obtained for specimens hardened in such a way reflects adequately the dynamics of these processes. In particular, the characteristic scale of the nitrogen diffusion in α -titanium for specimens cooled from $T = 1300$ K to 350 K is not more than 1 μm .

2. Experimental Results. In the experiments with simultaneous measurement of temperatures T_2 and T_1 on the surface and at the center of specimens, respectively, and also the nitriding process "hardening" it was found that over the whole heating rate range ($U = 50$ -500 K/sec) the ignition mode was realized. This is proved by both the time dependence of the surface-center temperature difference $\Delta T = T_2 - T_1$ (curve 1, Fig. 1b) and the cross-sectional distribution of nitrogen concentrations C_N in the "hardened" specimen (curve 2, Fig. 1b).

The dependences of the ignition delay time t_d measured from the external heating cessation moment to the temperature discontinuity (see Fig. 1) on the heating rate u , relative porosity θ , nitrogen pressure P , heating temperature T_h , and the composition of dilution of titanium by titanium nitride were found. Then, the variations of the specimen microstructure, particle morphology, and phase composition at all the ignition process steps can be followed.

2.1. Specific Features of Titanium Ignition in a Nitrogen Atmosphere. Figure 2a (curve 1) shows the relation $t = F(\theta)$ over the relative porosity range $\theta = 0.7$ -0.4 at constant process parameters ($P = 0.1$ MPa, $u = 45$ K/sec and $T_h = 1580$ K). It can be seen that as θ varies from 0.7 to 0.5, the ignition delay time triples. The maximum (max $t_d/d\theta$) is observed within the range $\theta = 0.7$ -0.65, that is, at the initial compaction stage.

Figure 2b shows the relation $t_d = F(T_h)$ (curve 1) at $P = 0.1$ MPa, $\theta = 0.5$, $u = 50$ K/sec. The results obtained show a fall of t_d with growth of T_h and existence of the critical temperature in the given conditions under which the specimen cannot be ignited and they coincide qualitatively with the data reported in [10]. It should be noted that the reaction depth ($\eta = \Delta m/m_0$) decreases as T_h rises (curve 2).

It is shown that as the nitrogen pressure varies in the range of 0.1 to 1 MPa at constant $T_h = 1600$ K and $u = 40$ K/sec, the ignition delay time is independent of the gas pressure. It is found that at $P > 0.1$ MPa t_d tends to decrease with a decrease of P (Fig. 2c). An attempt to detect the lower inflammation limit at the nitrogen pressure up to $P = 0.05$

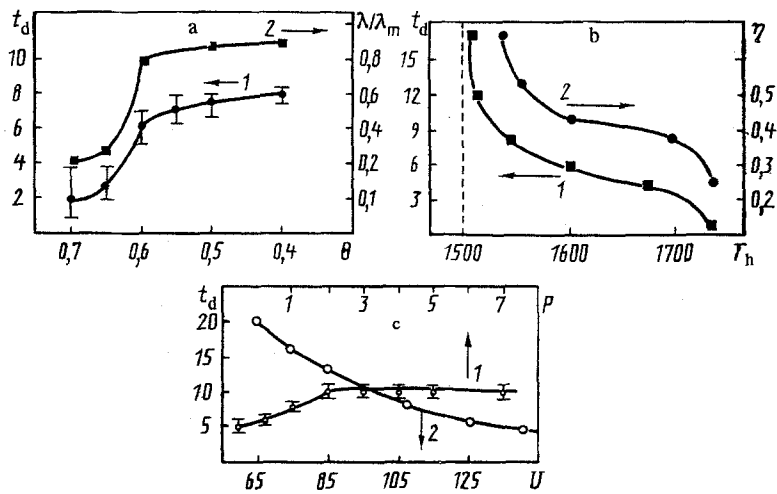


Fig. 2. Influence of the relative porosity θ (a, curve 1), maximum temperature T_h , K (b, curve 1), heating rate u , K/sec (c, curve 2), and nitrogen pressure $P \cdot 10$, MPa (c, curve 1) on the ignition delay time t_d , sec; the dependences of thermal conductivities λ/λ_m of compacted specimens on θ (a, curve 2) and the reaction depth $\eta = \Delta m/m$ on T_h (b, curve 2).

MPa failed. Ignition followed by combustion takes place at $P < 3 \cdot 10^{-2}$ MPa but at lower P the partial pressure of nitrogen P_N becomes comparable with the oxygen partial pressure P_O : the product synthesized is oxynitride and in our opinion these results cannot be considered in one series with the data obtained at $P_N/P_O \gg 1$.

In a wide range of dilution of the initial composition with titanium nitride (TiN) of 2 to 50 mass. % at $\theta = 0.5$, $u = 40$ K/sec, and $T_h = 1550$ K, $t_d \sim 10$ sec remains unchanged. This is not consistent with a strong dependence of the combustion rate in this system on dilution with the final product [3]. The absence of filtration hindrances in the titanium ignition process in nitrogen atmosphere is evidently the reason for this effect.

An interesting result on variation of t_d with increase of specimen heating rate was obtained (Fig. 2b, curve 2). At constant P , θ , and T_h (e.g., 1550 K) the ignition delay time decreased from 20 to 5 sec as u rose.

2.2. Structure Formation Trends. Let us consider the processes which take place at the microstructural level in a specimen "hardened" at different time steps t_i (i increases as the temperature discontinuity moment approaches) preceding or immediately following ignition.

Figure 3a ($\times 400$) shows the characteristic microstructure of the initial titanium specimen surface (t_0). Two main particle morphologies – large fragments and fine dendrites – can be seen. Compaction deformation of some of their surfaces can be observed.

A specimen particle surface at the time t is shown in Fig. 3b ($\times 10,000$). Numerous craters with a diameter of 0.2 μm are detected. The peculiarities associated with the surface deformation disappeared completely. This is accompanied by specimen mass losses of 2.5-3.0 mass. %.

At the subsequent time moment t_2 in the vicinity of craters and over their periphery new phase "nuclei" develop (Fig. 3c, $\times 4800$). The LRSA method revealed that they contained only two elements: nitrogen and titanium (the oxygen content is at least lower than 0.01 mass. %). It should be noted that nitride is located extremely irregularly both at the single particle level and over the whole specimen surface. It was found that initially the phase developed mainly in places of mutual particle overlapping, on concave surfaces (Fig. 3d, $\times 7000$) etc., that is, in regions least accessible to outside heat transfer. An attempt to find the trends in its distribution over the specimen macrosurface failed. Evidently, it may be attributed to inhomogeneity of the thermophysical properties of the heterogeneous medium.

Figure 3e ($\times 400$) shows a specimen surface microstructure at the time moment t_d (cf. Fig. 3a). It can be seen that TiN phase isles were formed on almost all the particles and their geometrical shape remained similar to the initial one.

An attempt "to stop" the process at the subsequent time moment t_4 failed, partly because of the finite nitrogen evacuation rate from the gaseous space and partly because of a low combustion limit for the nitrogen pressure in the

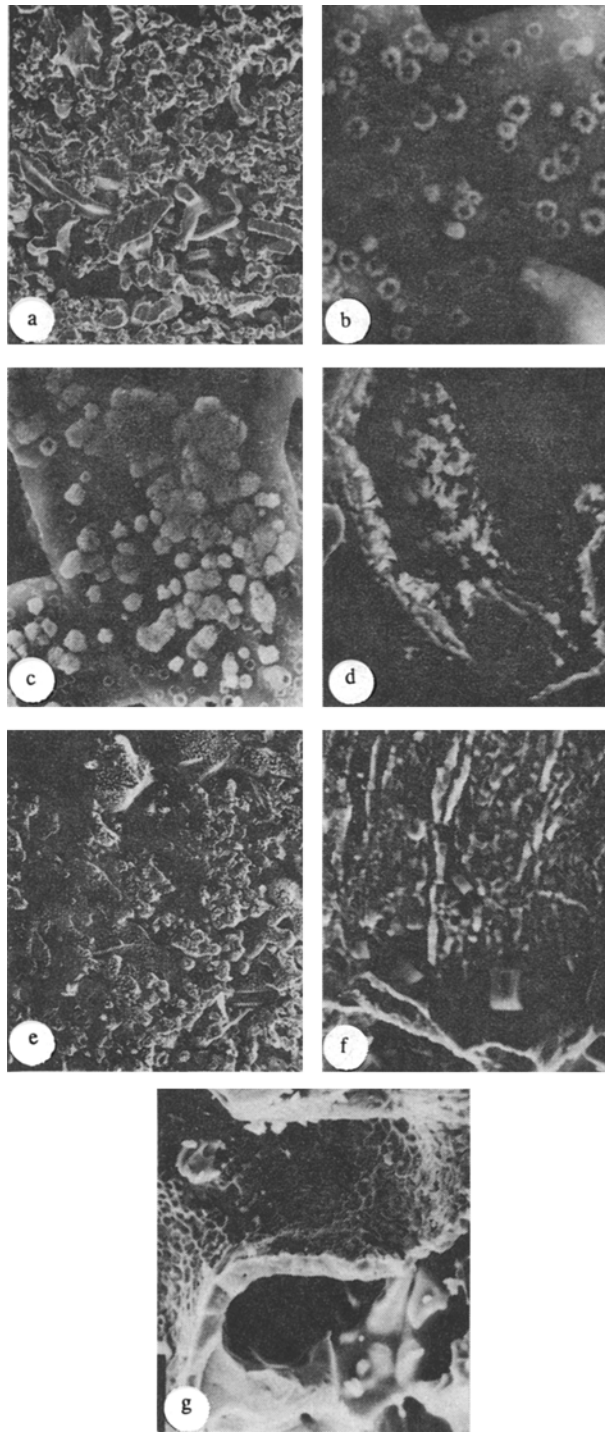


Fig. 3. Characteristic microstructures of titanium powder at different heat treatment moments.

Ti–W system. A microanalysis of the specimen section showed that after ignition the combustion wave spread toward the center over a distance of 800-1000 μm (see Fig. 1b). In Fig. 3f ($\times 5000$) the particle surface microstructure is shown 0.2-0.5 sec after inflammation. It should be noted that the product "film" is not solid and that the particle geometrical macroshape remains unchanged although, as was shown by measurements, the specimen surface particles remained there for ~ 0.15 sec at $T > T_m(\text{Ti})$. The RPA has shown that at that stage only TiN is formed.

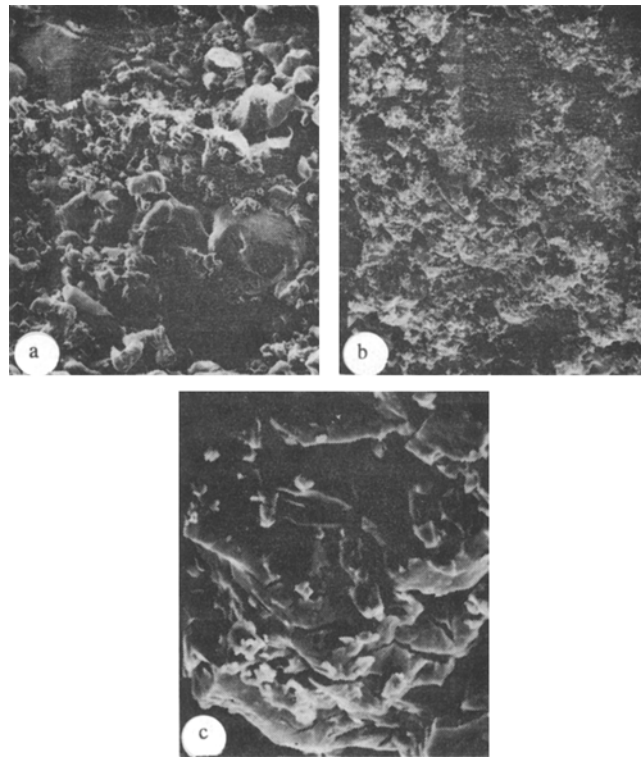


Fig. 4. Dispersion of titanium particles as a result of rapid heating: a ($\times 400$): initial powder; b ($\times 400$) and c ($\times 4000$): after pulse heating ($u = 300$ K/sec).

The characteristic microstructure of the final product obtained in combustion under natural conditions (without "hardening") is shown in Fig. 3g ($\times 4000$). It is seen that its formation is connected with melting and melt crystallization processes. Together with the TiN phase α, β -solid solution in Ti appeared. It should be noted that such a microstructure usually takes place at a distance of $> 1000 \mu\text{m}$ from the specimen surface and on the surface itself if the temperature of the second heating wave reaching it (Fig. 1, point B) is higher than the titanium melting point.

Another effect connected with changes of the specimen microstructure in the process of thermal treatment must be considered. To do this, we take again the specimens corresponding to times t_0 and t_1 . While earlier we followed the changes on Ti particles belonging to the specimen surface, now Fig. 4 shows the morphology of particles located inside the specimen at a distance of about $1000 \mu\text{m}$ from the surface. Comparative analysis of Figs. 4a (t_0) and 4b (t_1) shows that the average size of the initial particles is larger than for the specimen after heating. The effect observed is associated with particle cracking in the heating wave (Fig. 4b) and the larger the heating rate U , the more intensive the process.

3. Discussion. In this section, by correlating the conventional ignition thermal parameters with the observed microstructural changes, an attempt was made to describe consistently the physical and chemical processes which take place at the first stage of titanium–nitrogen interaction in the combustion wave and to correlate them with the ignition trends.

Constancy of t_d under a pressure varying over the wide range of 0.1 to 1 MPa (Fig. 2c) and a low inflammation limit for the pressure of the gas phase reagent ($P < 0.01$ MPa) suggest the absence of filtration hindrances to specimen ignition under the given experimental conditions. This conclusion is confirmed by studies of the microstructure and phase composition of "hardened" specimens, which showed that the first stage of chemical titanium–nitrogen interaction took place in a thin ($100\text{--}200 \mu\text{m}$) near-surface layer of the specimen. Moreover, the effects of decreasing t_d with a decrease of P ($P < 0.01$ MPa) and specimen mass losses found simultaneously indicate the importance of gas phase processes of the Ti (solid) \rightarrow Ti (293) type at the first ignition stages ($t_0 - t_1$). This conclusion is completely consistent with REM data (Fig. 3b) proving that "crater formation" on the titanium particle surfaces is predominant and possibly a key factor at the first stage of nitride phase development and its "nuclei" are localized mainly on the periphery of these formations.

At subsequent time moments ($t_2 - t_1$) the heterogeneous titanium nitride phase formation reaction occurs in the form of isolated regions both on the "crater" circumferences and over the whole particle surface (Fig. 3c). It seems important to consider here the discovered inhomogeneity of the new phase formation (Fig. 3d). This effect can manifest itself at two levels: micro, on the surface of a single particle and macro, on the surface of the whole specimen. It seems to be caused by thermal inhomogeneity of the heterogeneous system, which may be a result of a different number of contacts per particle.

These microstructural effects correlate with results obtained from the relation between t_d and specimen porosity (Fig. 2b, curve 1). It is shown that at large θ there is a great scatter in t_d values. At large porosities the probability is increased that different Ti particles or their different "microregions" will be at different heat removal conditions.

It is also found that at large θ the "nuclei" densities on the particles within the surface layer are higher. In view of the fact that in such experimental conditions no filtration hindrances can arise (Fig. 2c), the only explanation of the tendency observed is the influence of changes in the thermal conductivity λ/λ_m of the disperse system skeleton caused by changes of its porosity on the ignition process. In Fig. 2a the variation of λ/λ_m with compacted-powder porosity is shown (curve 2). This relation correlates with the relation of t_d with θ (curve 1); in particular, its maximum also falls within the θ range of 0.7-0.65.

In the subsequent interval ($t_3 - t_2$) there is an increase of the density of formation of the nitride isles up to a certain critical value, followed by ignition, that is, an abrupt increase of the TiN phase formation rate. It should be noted that before the temperature discontinuity moment in the surface layer there is one more structural effect: cracking of titanium particles located at a depth of 150-200 μm from the surface. It may be ascribed to the existence of substantial thermal stresses in the particles at large heating rates. It is known [9] that only a few tenths of a weight percent of impurities including nitrogen, which form solid implantation solutions bring the titanium forgeability practically to zero. Therefore it may be suggested that at temperature gradients of about 10^2 - 10^3 K/sec brittle titanium particles of solid nitrogen solution (~ 0.1 wt. %) in titanium crack.

The observed dependence of the ignition delay time on the heating rate may be explained by the same effect (Fig. 3i, curve 2). With an increase of the heating rate (consequently, an increase of the temperature gradients) release of new reactive surfaces occurs more intensely due to particle cracking, which, in turn, increases the rates of nitrogen absorption and nitride phase formation and decreases the time needed to achieve the critical density of the nitride phase. In [10] in the explanation of the change of this dependence during transition from self-ignition to titanium ignition in an air atmosphere it was suggested that the process might be influenced by the structural effect of cracking the oxide film decelerating the process but microstructural studies were not conducted.

The microstructure of the "primary" product obtained after ignition (t_4) is shown in Fig. 3e. In spite of the fact that the specimen surface temperature was higher than the titanium melting temperature $T_{m,Ti}$, the particle morphology coincides with the initial one (cf. Fig. 3a) and only very thorough examination reveals considerable changes of the surface topography (Fig. 3f). In this case RPA shows existence of a single nitrogen-containing phase TiN. In general, this phase film is not solid. A different situation is observed when a combustion wave from the bulk of the burning specimen gets to the surface (wave B, Fig. 1a). In this case "primary" particle cracking, flowing out of nonreacted titanium, and dissolution of TiN and nitrogen films in it are observed. The final-product microstructure shown in Fig. 2g is formed. This effect manifests itself on the surface more strongly, the higher the second-wave temperature; the structure formed and its phase composition are similar to those in the central part of the specimen burnt up under "natural" SHS combustion.

CONCLUSION

A study of the structure- and phase-formation processes and ignition parameters in rapid pulse heating of titanium specimens in a nitrogen atmosphere showed the following results.

1. It is found that the initial stages of the preexplosive titanium-nitrogen interaction mechanism involve titanium transformation into a gas phase with subsequent heterogeneous reaction.
2. It is shown that titanium nitride is a primary product and its production induces inflammation of the heterogeneous medium.
3. At all the steps of the process studied the effect of micro- and macrohomogeneous formation of the primary-product microstructure is found. This effect influences the ignition parameters.

4. The effect of ignition delay time reduction with increase of the specimen heating rate is found; it is shown that this effect is connected with dispersing solid phase reagent particles.

5. It is shown that the microstructure and phase composition of the primary products formed in the steady-state combustion wave and in the transition inflammation process are identical.

The authors are sure that the data obtained will be useful for better understanding of the formation processes that take place in combustion of hybrid metal-nitrogen systems and will be used for solution of the problem of controlling the SHS ceramic material microstructure.

NOTATION

t, time; S, specific surface of powder; d, particle diameter; U, heating rate; P, gaseous-medium pressure; T, temperature; T_h , maximal heating temperature; θ , relative porosity; t_d , ignition delay time; λ , thermal conductivity; η , reaction depth; C_N , mass concentration of nitrogen; h, r, specimen height and radius; m_0 , Δm , initial specimen mass and its changes after combustion.

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