SOME PRINCIPLES OF COMBUSTION OF TITANIUM—SILICON MIXTURES

T. S. Azatyan, V. M. Mal'tsev,
A. G. Merzhanov, and V. A. Seleznev

In the present work optical methods are employed to study the combustion of mixtures of titanium with silicon. The combustion of such mixtures, like that of titanium—carbon [1] and titanium—boron [2] mixtures, is of the "gasless" combustion type. Calculations of the adiabatic temperature [3] have shown that the combustion temperature of a titanium—silicon mixture with composition Ti—0.6Si (T_{ad} = 2500°K) is less than the combustion temperatures of titanium—carbon mixtures (T_{ad} = 3200°K, composition Si—C) and titanium—boron mixtures (T_{ad} = 3200°K, composition Ti—2B).

The mechanism of combustion of titanium—silicon mixtures was studied in [4], wherein it was demonstrated that in the combustion regime silicides of various modifications can be obtained (Ti_5Si_3, TiSi, $TiSi_2$), with the combustion products being either single phase or multiphase, depending on the combustion conditions. Studies have shown that the combustion rate of these mixtures depends on the density and diameter of the specimens, the size of the titanium particles, the dilution of the mixtures by the final products, and the ratio of metal to nonmetal (the coefficient α) in the original mixture. However, data on the relationship of the maximum combustion-wave temperature to these parameters are not available in the literature.

Pressed specimens were heated in a constant-pressure vessel and an inert argon atmosphere at a pressure of 10 atm. The relative density of the cylindrical specimens was 0.65, and their diameter was 15 mm. Type PTS titanium ($r \leqslant 280$ μm) and semiconductor silicon ($r < 30$ μm) were used in the experiments. The combustion-wave propagation rate was determined photographically [5], while the temperature was determined by a method based on the measurement of radiation intensity at a series of wavelengths [6, 7], the uncertainty in temperature measurement not being worse than ±80°.

EFFECT OF THE COEFFICIENT α ON MAXIMUM COMBUSTION TEMPERATURE

A method of calculating the adiabatic combustion temperature in the combustion wave at various values of α was presented in [3]. The calculated temperature was determined with the assumption of complete transformation and absence of heat loss, so that in a number of cases the calculated temperature differs from the true temperature developed in the combustion wave.

Figure 1 shows the dependence of the calculated adiabatic and experimentally measured maximum combustion-wave temperatures for a titanium—silicon mixture on α ($r \leqslant 45$ μm). The highest value — T_{max} = 2360°K — corresponds to a Ti—0.6Si mixture. According to the data of [4], at α = 0.6, the combustion product consists of single phase Ti_5Si_3. For α < 0.6 the end product is Ti_5Si_3 and unreacted titanium remains; at α > 0.6, during the combustion process three phases are formed simultaneously: Ti_5Si_3, TiSi, and $TiSi_2$. The decrease in T_{max} at α > 0.6 is produced by the formation of the silicides TiSi (T_{ad} = 2000°K) and $TiSi_2$ (T_{ad} = 1800°K) with lower adiabatic temperature values than in Ti_5Si_3 formation. The absence of quantitative phase ratio data for α > 0.6 prevents calculation of adiabatic temperatures at these α values.

In contrast to the previously studied titanium—carbon system [8], in the combustion of titanium—silicon mixtures isothermal segments can be found in the temperature profiles.

We will consider the composition Ti—0.5Si (T_{max} = 2230°K), on the temperature profile of which there is a segment where the reaction occurs isothermally (Fig. 2a, curve 2), corresponding to T = 1970°K. The appearance of this segment is evidently connected with the melting of titanium (T_f = 1950°K). With increase in the quantity of Ti in the original mixture (α = 0.45), T_{max} decreases (2080°K), and the segment wherein the reaction occurs isothermally expands. Thus, at α = 0.5, its width is ~0.2 mm, and at α = 0.45, it is ~0.5 mm.

Moscow. Translated from Fizika Goreniya i Vzryva, Vol. 15, No. 1, pp. 43-49, January-February, 1979. Original article submitted January 19, 1978.

0010-5082/79/1501-0035$07.50 © 1979 Plenum Publishing Corporation

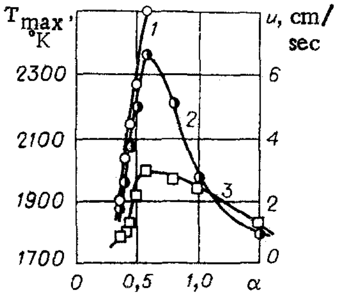

Fig. 1. Calculated adiabatic (1) and experimentally measured (2) temperatures and combustion-wave propagation rate (3) of a titanium—silicon mixture versus coefficient α.

At α = 0.4, the maximum combustion temperature (1960°K) approaches the melting point of titanium.

A theoretical description of gasless combustion with phase transformations of the reagents and materials formed was performed in [9, 14], and it was shown that phase transformations in the combustion wave may be accomplished in both the Stefan and chemical transformations regimes. In the first regime phase conversion occurs because of the thermal flux from the higher temperature region of the combustion wave, with temperature then rising continually (elementary combustion model of the first sort, ÉCM-1). In the second regime there is a segment where the reaction occurs isothermally, screening the thermal flux from the maximum temperature zone (ÉCM-2). The latter regime is realized at phase transition temperatures close to the combustion temperature.

At α = 0.6, when the components are completely expanded in the reaction (stoichiometric composition), titanium fusion occurs in the Stefan regime [14], and there is no isothermal segment in the temperature profile. For the cases α = 0.5 and 0.45 (excess titanium content), there occurs a second titanium fusion regime. In the composition Ti—Si (α = 1, r < 63 μm, T_{max} = 1960°K), there is also an isothermal segment ~0.2 mm in width, corresponding to T = 1800°K (see Fig. 2b, curve 1). Its appearance is evidently related to fusion of the phase $TiSi_2$ (the $TiSi_2$ fusion temperature is 1770°K), which is formed by combustion. Increase in the Ti particle size to 90 μm has no significant effect on the temperature of the isothermal segment, but does lead to its expansion to ~0.4 mm and to an insignificant decrease in the value of the maximum combustion temperature (Fig. 2b, curve 2). Thus, at $63 \leqslant r \leqslant 90$ μm, T_{max} = 1910°K. Upon addition to the Ti—Si mixture ($63 \leqslant r \leqslant 90$ μm) of 10% of the final product obtained by the combustion of a Ti—Si composition ($r \leqslant 63$ μm), the maximum combustion temperature (1790°K) approaches the fusion temperature of $TiSi_2$ (Fig. 2b, curve 3). Since at α = 0.6 the final product is single phase, below the effect of titanium particle size, dilution of the original mixture by the final product, and density of the pressed specimens on combustion temperature will be considered basically for the system Ti—0.6Si.

EFFECT OF TITANIUM PARTICLE SIZE ON MAXIMUM COMBUSTION TEMPERATURE

Experimental measurements of the combustion temperature at various values of titanium particle size have shown that with increase in r, the temperature decreases (Fig. 3, curve 1) together with the combustion rate (Fig. 3, curve 2). In [3], it was demonstrated that with increase in particle size there is not only a decrease in combustion rate, but also a change in phase composition of the final product. Thus, in combustion of titanium particles with $r \leqslant 45$ μm, the final product is single phase Ti_5Si_3, while at $r \geqslant 100$ μm instead of Ti_5Si_3 the final product contains $TiSi_2$ and unreacted titanium. The decrease in combustion temperature in this case is explained not only by the increase in the degree of non-burnup (the quantity of unreacted components), but also by the formation of the low-temperature phase $TiSi_2$ in the combustion wave.

The temperature profile of the composition Ti—0.6Si ($125 \leqslant r \leqslant 1600$ μm, T_{max} = 2120°K) is of interest, showing two isothermal segments (see Fig. 2c, curve 1). The first segment

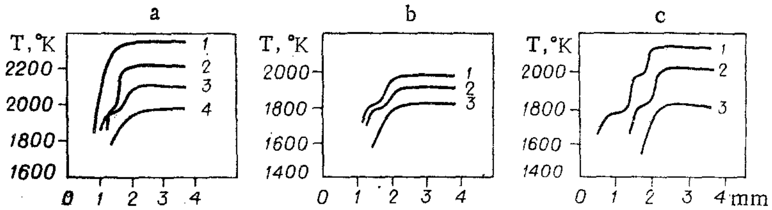

Fig. 2. Temperature distribution over the combustion wave for a titanium—silicon mixture versus α and r. a) $r \leqslant 45$ μm: 1) $\alpha = 0.6$; 2) $\alpha = 0.5$; 3) $\alpha = 0.45$; 4) $\alpha = 0.4$; b) $\alpha = 1$: 1) $r \leqslant 45$ μm; 2) $63 \leqslant r \leqslant 90$ μm; 3) $63 \leq r \leq 90$ μm, $\sigma = 10\%$; c) $\alpha = 0.6$: 1) $125 \leqslant r \leqslant 160$ μm; 2) $160 \leqslant r \leqslant 180$ μm; 3) $180 \leqslant r \leqslant 200$ μm.

at T = 1760°K (width ~0.4 mm) evidently corresponds to melting of $TiSi_2$; the second segment at T = 1970°K (width ~0.3 mm) is close to the titanium melting point. With increase in titanium particle size from 160 to 180 μm (Fig. 2c, curve 2), T_{max} (1980°K) does not exceed the T_f of Ti, and the isothermal segment (T = 1800°K) with width ~0.3 mm is close to T_f of $TiSi_2$. With increase in titanium particle size from 180 to 200 μm, the combustion temperature does not exceed the melting point of $TiSi_2$ (T_{max} = 1800°K) (Fig. 2c, curve 3). At $r \geqslant 200$ μm, a clearly defined autooscillatory combustion regime is found.

On the basis of the results obtained, in the combustion of titanium—silicon systems we can distinguish the following cases, corresponding to the various mechanisms for the process:

1) Combustion of fine titanium particles ($r \leqslant 45$ μm, $\alpha = 0.6$). The single-phase product Ti_5Si_3 is formed, and the reagents are expended completely. The combustion temperature* (T_{max} = 2360°K) is close to the melting point of the final product (the melting point of Ti_5Si_3 is 2390°K), and both components in the reaction zone are in the liquid state (T_{fTi} = 1950°K, T_{fSi} = 1690°K). Here, evidently, mutual diffusion of the reagents in the liquid state predominates, and combustion occurs in the Stefan regime (elementary combustion model of the first sort).

2) Combustion of fine titanium particles ($r \leqslant 45$ μm, $\alpha < 0.6$). The final product is Ti_5Si_3, and unreacted titanium also appears. In the temperature profile of these compositions there is an isothermal segment corresponding to titanium fusion. Combustion occurs in the chemical transformation regime (elementary combustion model of the second sort).

3) There is a case for compositions, the combustion of which produces a multiphase final product. Thus, at $r \leqslant 45$ μm and $\alpha = 1$ the original reagents are expended completely and the phases Ti_5Si_3, $TiSi_2$, and TiSi are formed; in the temperature profile, there is an isothermal segment corresponding to the melting of the phase $TiSi_2$. At $125 \leqslant r \leqslant 200$ μm the phases Ti_5Si_3, $TiSi_2$, and residual unreacted titanium are produced. In the temperature profile of this composition there are two isothermal segments, corresponding to the melting of $TiSi_2$ and Ti. Here, evidently, solution of titanium in the $TiSi_2$ solution produced predominates, leading to saturation of the titanium solution and formation of Ti_5Si_3.

With titanium particle sizes $250 \leqslant r \leqslant 280$ μm in the mixture ($\alpha = 1$, $\rho = 0.7$, d = 10 mm) spin combustion is observed (Fig. 4). Spin effects in the combustion of solid systems were first described in [11] and studied in detail in [12]. They are usually observed in the combustion of titanium, zirconium, and hafnium mixed with nitrogen and argon. The spin combustion observed in the present study in a Ti—Si mixture is unstable, changing at certain points into an autooscillatory combustion regime and then developing anew. During specimen combustion there are often brightly scintillating points moving in one and the same direction or towards each other. The parameters of the process are mean combustion rate $u \simeq 0.6$ cm/sec, velocity of displacement of bright light-emitting points $u_p \simeq 10$ cm/sec, and mean rotation frequency $\nu = 3.5$ sec^{-1}. It should be noted that the surface of the combusted specimen and its cross sections are homogeneous, while in combustion of metals in nitrogen traces of the spin combustion usually remain in the burned up specimen. The mechanism for the development of spin combustion during the burning of solid reagents remains to be studied.

---

*Measurements of the combustion temperature of a mixture with $r < 45$ μm at $\alpha = 0.6$ were performed by the thermocouple method in [10] (T_{max} = 2350°K).

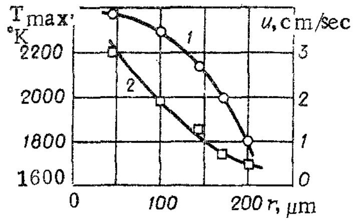

Fig. 3

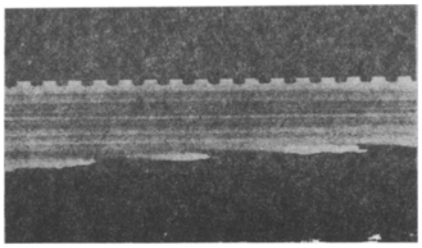

Fig. 4

Fig. 3. Maximum temperature (1) and combustion-wave propagation rate (2) of a titanium–silicon mixture versus titanium particle size.

Fig. 4. Photogram of spin combustion regime for a titanium–silicon mixture.

EFFECT OF DILUTION OF INITIAL MIXTURE BY FINAL PRODUCT ON MAXIMUM COMBUSTION TEMPERATURE

A thermodynamic calculation has shown that with increase in concentration of the final product σ in the initial mixture the adiabatic temperature in the combustion wave decreases. Figure 5 shows the dependence of the calculated adiabatic (without consideration of heat of fusion) and experimentally measured temperature versus σ for Ti–0.6Si ($r \leqslant 45$ μm). The size of the diluent particles was $\leqslant 63$ μm. According to the data of [4], the phase composition of the combustion products remains constant at all levels of dilution and corresponds to the silicide Ti_5Si_3 (reagents are expended completely). No isothermal segments were observed in the temperature profiles of the compositions considered.

EFFECT OF SPECIMEN DENSITY ON MAXIMUM COMBUSTION TEMPERATURE

It was noted previously that the combustion rate of titanium–silicon mixtures depends on the density of the pressed specimens. The investigations performed in the present study reveal that the dependence of the combustion rate of a Ti–0.6Si mixture ($r \leqslant 45$ μm) has a weakly expressed maximum (Fig. 6). The function $T_{max} = f(\rho)$ saturates at $\rho \geqslant 0.6$. The increase in temperature and combustion rate with increase in ρ is evidently produced by improved contact between the reacting components and increase in the completeness of transformation in the synthesis wave. At $\rho = 0.7$–0.8, heat loss from the reaction zone begins to have an effect because of increase in thermal conductivity ($u \sim 1/\sqrt{\rho}$).

According to the data of [4], with change in ρ from 0.41 to 0.62, the degree of non-burnup changes insignificantly (the quantity of free silicon changes by 0.08%). This is also indicated by the weak dependence of maximum temperature over the ρ range studied (Fig. 6, curve 1).

RELATIONSHIP OF COMBUSTION-WAVE PROPAGATION RATE TO TEMPERATURE AND CONVERSION DEPTH

The relationship between u, T_*, and η_* was presented in [9] in the form

$$u^2 = \frac{\lambda}{Q\rho} \cdot \frac{RT_*^2}{E} \frac{k_0 e^{-E/RT_*}}{f(\eta_*)}.$$

where η_* is the conversion depth; λ is the thermal conductivity coefficient, cal/(cm·sec·deg); Q is the heat of formation of the product, kcal/mole; ρ is the density, g/cm^3; E is the activation energy, kcal/mole; and k_0 is the preexponent. For the elementary combustion model of the first sort, $T_* = T_{max}$ (the maximum combustion temperature) and

$$f(\eta_*) = \int_0^1 \frac{1-\eta}{\varphi(\eta)} d\eta,$$

where $\varphi(\eta)$ is the kinetic function. For the elementary combustion model of the second sort, $T_* = T_f$ (phase-transition temperature) and

$$f(\eta_*) = f(\eta_f) = \int_0^{\eta_f} \frac{\eta_f - \eta}{\varphi(\eta)} d\eta.$$

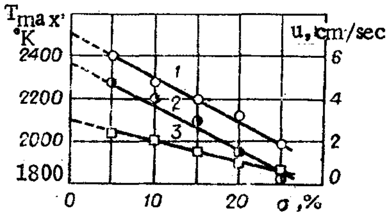

Fig. 5

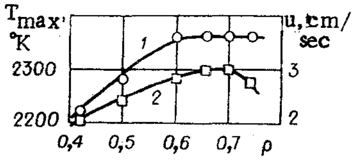

Fig. 6

Fig. 5. Calculated adiabatic (1) and measured maximum (2) temperatures and combustion-wave propagation rate (3) in a titanium–silicon mixture versus diluent concentration.

Fig. 6. Maximum temperature (1) and combustion-wave propagation rate (2) of a titanium–silicon mixture versus specimen density.

TABLE 1

α	ν, %	u, cm/sec	η_f
0,52	11,38	2,2	0,80
0,5	12,9	1,7	0,84
0,48	15,61	1,6	0,89
0,47	16,98	1,4	0,93
0,45	20,02	1,2	0,96

Previously, the elementary combustion model of the second sort has been observed in an Ni–Al system in [13], where the form of the function $\varphi(\eta)$ was determined by establishing the dependence of u on η_f. The method proposed there was used in the present study to determine $\varphi(\eta)$ for the case of the interaction of titanium with silicon.

We will consider the composition Ti–αSi ($\alpha \leqslant 0.6$, $r \leqslant 45$ μm), where the silicide Ti_5Si_3 is formed and residual titanium remains. At $\alpha = 0.6$, as mentioned above, there is no isothermal segment in the temperature profile. The value of α at which the phase transition still occurs in the Stefan regime proves to be 0.55 at $T_{max} = 2270$°K $\simeq T^{cr}_{max}$. With reduction in the maximum combustion temperature by decreasing α from 0.25 to 0.45, there appear isothermal segments, and the chemical transformation regime occurs, i.e., T^{cr}_{max} is the lowest value of T_{max} at which the phase transition is still accomplished in the Stefan regime. At $\alpha \leqslant 0.4$, the combustion temperature T_{max} does not exceed the melting point of titanium.

The conversion depth (η_f) at the commencement of the phase transition is determined from the expression

$$3(1-\eta_f)\,\Delta H_{Si}(T_f)+(5-5\eta_f+m)\,\Delta H_{Ti}(T_f)+\eta_f\,\Delta H_{Ti_5Si_3}(T_f)=Q\eta_f,$$

where $m = (3-5\alpha)\alpha = \nu/(1-\nu)\cdot\mu_{Ti_5Si_3}/\mu_{Ti}$; μ is the molecular weight; and ν is the fraction of excess titanium in the original mixture. The dependence of η_f on α is shown in Table 1. Figure 7 shows the function $u(\eta_f)$, which can be regarded as well defined and represented by the formula

$$u = a\cdot\eta_f^{-m},$$

where $a = 1$ cm/sec; $m = 3$. Thus on the basis of experimental data, $f(\eta_f) = \eta_f^3$, and the kinetic function $\varphi(\eta) = \eta^{-1}$, which corresponds to a parabolic interaction law for the components [9].

We will now consider the relationship between the combustion rate and temperature upon dilution of a Ti–0.6Si mixture ($r \leqslant 45$ μm) by the final product. Since in this case the elementary combustion model of the first sort occurs, the combustion rate is determined by the maximum temperature developed in the wave. Figure 8a shows the function $u = u(T_{max})$ for the composition under consideration at various σ values. Points are superposed on this function corresponding to combustion of the composition Ti–αSi ($r \leqslant 45$ μm at $\alpha = 0.55$; 0.6 and $\alpha = 0.4$; 0.36), where isothermal segments are absent and the combustion rate is determined

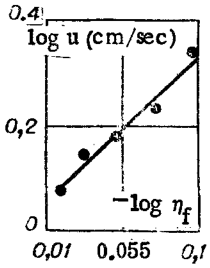

Fig. 7

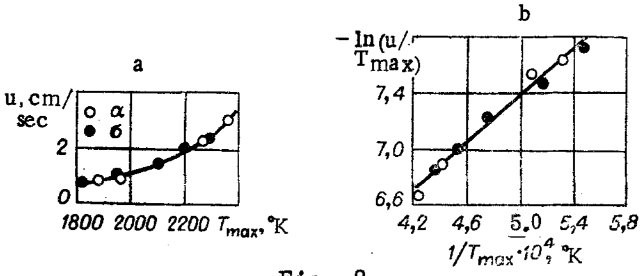

Fig. 8

Fig. 7. Combustion rate u versus η_f.

Fig. 8. Relationship between the combustion rate and maximum temperature at various α and σ.

by T_{max}. This is evidently explained by the fact that upon combustion of the mixtures under consideration, the single-phase product Ti_5Si_3 is formed, and the reaction $5Ti + 3Si \rightarrow Ti_5Si_3$ is responsible for the temperature and wave-propagation rate. Since the dependence of $\ln(u/T_{max})$ on $1/T_{max}$ is linear (Fig. 8b), the activation energy of this reaction can be calculated, proving to be equal to 30 kcal/mole.

Thus, the present study has considered the effect of various parameters on the combustion temperature of titanium–silicon mixtures. It has been shown that for the given system the processes that occur are characteristic of the elementary combustion model of the second sort. On the basis of experimental data, the form of the kinetic function of the titanium–silicon interaction and the activation energy of the reaction $5Ti + 3Si \rightarrow Ti_5Si_3$ have been determined.

The authors thank V. M. Maslov for his valuable advice and evaluation of the study.

LITERATURE CITED

1. V. M. Shkiro and I. P. Borovinskaya, in: Combustion Processes in Chemical Technology and Metallurgy [in Russian] (edited by A. G. Merzhanov), Chernogolovka (1975).
2. I. P. Borovinskaya, A. G. Merzhanov, et al., Fiz. Goreniya Vzryva, 10, No. 1 (1974).
3. N. P. Novikov, I. P. Borovinskaya, and A. G. Merzhanov, in: Combustion Processes in Chemical Technology and Metallurgy [in Russian] (edited by A. G. Merzhanov), Chernogolovka (1975).
4. A. R. Sarkisyan, S. K. Dolukhanyan, et al., Fiz. Goreniya Vzryva, 14, No. 3 (1978).
5. P. F. Pokhil, V. M. Mal'tsev, and V. M. Zaitsev, Methods for Study of Combustion and Detonation Processes [in Russian], Nauka, Moscow (1969).
6. T. S. Azatyan, V. M. Mal'tsev, et al., Fiz. Goreniya Vzryva, 10, No. 3 (1974).
7. T. S. Azatyan, V. M. Mal'tsev, and V. A. Seleznev, Fiz. Goreniya Vzryva, 12, No. 2 (1976).
8. T. S. Azatyan, V. M. Mal'tsev, et al., Fiz. Goreniya Vzryva, 13, No. 2 (1977).
9. A. G. Merzhanov, Dokl. Akad. Nauk SSSR, 233, No. 6, 1130 (1977).
10. V. M. Maslov, I. P. Borovinskaya, and A. G. Merzhanov, Fiz. Goreniya Vzryva, 14, No. 5 (1978).
11. A. G. Merzhanov, A. K. Filonenko, and I. P. Borovinskaya, Dokl. Akad. Nauk SSSR, 208, No. 4 (1973).
12. A. K. Filonenko and V. I. Vershinnikov, Fiz. Goreniya Vzryva, 11, No. 3 (1975).
13. V. M. Maslov, I. P. Borovinskaya, and A. G. Merzhanov, Fiz. Goreniya Vzryva, 12, No. 5, 703 (1976).
14. A. P. Aldushin and A. G. Merzhanov, Dokl. Akad. Nauk SSSR, 256, 1133 (1977).