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THERMAL ANALYSIS OF HIGH-SPEED HIGH-TEMPERATURE REACTIONS OF REFRACTORY CARBIDE SYNTHESIS

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A new thermoanalytikal method, called electrothermal explosion (ETE) is described in which uniform heating of samples at extremely high rates (up to 10^5 deg·sec^{-1}) is achieved. Heating is by direct passing of an electric current through the sample in the initial stages and by chemical heat release after the ignition conditions have been attained. ETE is the only direct method that allows the macrokinetics of heterogeneous reactions occurring in condensed systems to be studied at high temperatures and at short conversion times, which are prohibitive for traditional thermoanalytical devices (up to 3500 K and 10^{-2} sec respectively).

Kinetic data on high-temperature, high-speed interactions in powder mixtures of carbon with titanium, silicon and tantalum are presented.The rate of heat release in the Ti–C system depends only to a small extent on temperature after the metal has melted, being mainly determined by the solution rate of carbon particles. The interaction mechanism in the Si–C system is similar to that in Ti–C, but the high enthalpy of carbon solution in liquid silicon results in a bulk activation energy of $E = 55$ kcal·mol^{-1}. Synthesis of tantalum carbide from the elements in the temperature range 1500–3000 K occurs by the mechanism of reaction diffusion and proceeds with strong self-retardation.

Keywords: carbide synthesis, electrothermal explosion, high-speed high temperature reactions, kinetics

Introduction

To determine the causes of the main characteristics of self-propagating high-temperature synthesis (SHS) in mixtures of powders, it is necessary to know the kinetic parameters of mixture-component interaction over a wide temperature range, up to the combustion temperature, which can reach 3500 K [1]. Kinetic experiments at such high temperatures by classical isothermal methods (calorimetry, thermal gravimetry, etc.) are practically impossible, owing to the brevity of the corresponding processes (10–100 msec) as well as to fundamental difficulties in thermostatic control of the reaction mixture at such high temperatures.

A successful solution is that of using the electrothermal explosion (ETE) that occurs under heating of the reacting specimen by sending an electrical current through it [2, 3]. The reaction can thus be made to proceed uniformly throughout the volume, which allows quantitative calculation of the kinetic parameters from experimental thermograms. With specimen heating by conventional methods, i. e. through the external surface, the heating rate is limited by the need to equalize the temperature throughout the specimen and cannot exceed ≈ $\text{deg}\cdot\text{sec}^{-1}$. Volume heating of the specimen in the process of ETE development removes this limitation, and the heating rate can be 10^2–10^5 $\text{deg}\cdot\text{sec}^{-1}$.

In as much as uniform heating over the bulk of the sample is not always achieved during ETE, criteria are needed for selection of experimental data suitable for further analysis. For example, poor contact between sample and electrodes is responsible for non-uniform heating by electric current. As a result, a gas-less combustion wave develops along the sample Fig. 1a. It is difficult to assess the chemical heat release in such experiments since it is not known how thermal conductivity changes in the combustion wave.

Under uniform electrical heat release, the ETE regimes can differ radically with length of the sample. Temperature profiles along a short sample have a distinct maximum. The explosion takes place in the 'Frank–Kamenetsky regime' (Fig. 1b). In a longer sample, the explosion occurs in the 'Todes regime' without any noticeable temperature distribution (Fig. 1c). The latter is better suited for kinetic treatment.

The rise in specimen temperature T in ETE in the absence of external thermal losses is determined by the heat release from chemical reaction q_{ch} and electrical heating q_{el} [4].

$$c\cdot\rho\frac{\mathrm{d}T}{\mathrm{d}t}=\dot{q}_{\text{ch}}+\dot{q}_{\text{el}} \tag{1}$$

where c is specific heat, ρ is density, and t is time. The power of chemical heat release obeys the Arrchenius law and is an exponential function of temperature, while the electrical power changes insignificantly during an experiment. Therefore, there exists a temperature T_* at which these powers are equal. At temperatures $T<T_*$, the specimen is heated by electric current practically as an inert body; at $T>T_*$, the chemical heat release rises rapidly and determines completely the course of the process. At temperatures close to T_*, the power of chemical heat release is comparable with the electrical power and can be calculated from the present slope of the thermogram according to Eq. 1. For calculations of $\dot{q}_{\text{ch}}$ at temperatures that considerably exceed T_* [5], the term $\dot{q}_{\text{el}}$ must be assumed to be equal to zero. The calculations of $\dot{q}_{\text{ch}}$ is additionally simplified if the electric heating is turned off when the specimen temperature reaches $T=T_*$. Under these conditions, further self-heating of the specimen is due exclusively to chemical heat release. In the case of a single-stage process, the formula for the reaction rate $\dot{\eta}$ has the simplest form:

$$\dot{\eta} = \frac{\dot{q}_{\mathrm{ch}}}{Q} = \frac{c\cdot\rho}{Q}\frac{\mathrm{d}T}{\mathrm{d}t}, \tag{2}$$

where Q is the heat of reaction.

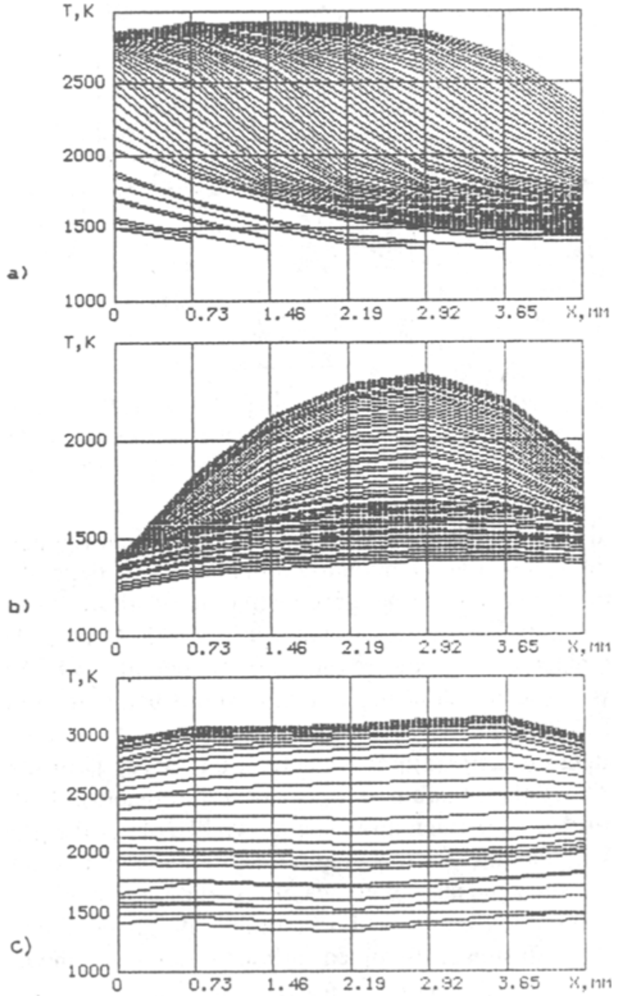

Fig. 1 Series of temperature profiles along a sample in consecutive moments of time (step 3.9 msec): *a*) combustion wave during sample heating by electric current; *b*) electrothermal explosion of the short sample (l = 5 mm); *c*) electrothermal explosion of long sample (l = 10 mm)

Results and discussion

The experimental set-up Fig. 2 used in the kinetic studies of interaction in powder mixtures during ETE comprised a powerful electric source and a temperature recording system. The data processing was carried out on-line by the computer. The main parameters of the set-up are as follows: power – 100 kW, range of temperature recording – 1000–3500 K, speed of response – 1.3 msec, space resolution of the temperature profile – 0.7 mm.

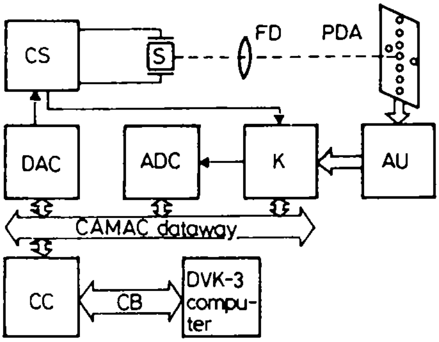

Fig. 2 Experimental configuration: CS) current source; S) specimen, FD) focusing device; PDA) photodiode array; AU) amplifier unit; K) commutator; ADC) analog-to-digital converter; DAC) digital-to-analog converter; CC) crate controller; CB) common bus

The potential of the ETE method is illustrated by a high-temperature study of the interaction of titanium and tantalum with carbon. The dependence of rate of chemical heat release on the temperature of titanium-carbon powder mixtures is given in Fig. 3 in the Arrhenius anamorphosis [3]. Before the experiment titanium-carbon black compacts were thermally treated at $T = 800^\circ C$, $t = 30$ min. The relationships presented show that at temperatures below the titanium melting point, the rate of titanium interaction with graphite and carbon black alike is strongly dependent on temperature: the activation energy is of the order of $E =$ 50 kcal/mole. Above the titanium melting point, the reaction is thermally inactivated and, as further experimentation has shown [7], obeys the pseudo-zero law.

It is most likely that the limiting step in this case is the dissolution of carbon in liquid titanium, since the macrokinetics of dissolution in metal melts is characterised by low activation energies. Furthermore, it can be shown that for the process limited by diffusion of dissolved carbon particles into the liquid titanium, the transformation law takes the form: $\dot{\eta} = (1 - \eta)^{1/3}$ and is close to the zero law for a wide range of η.

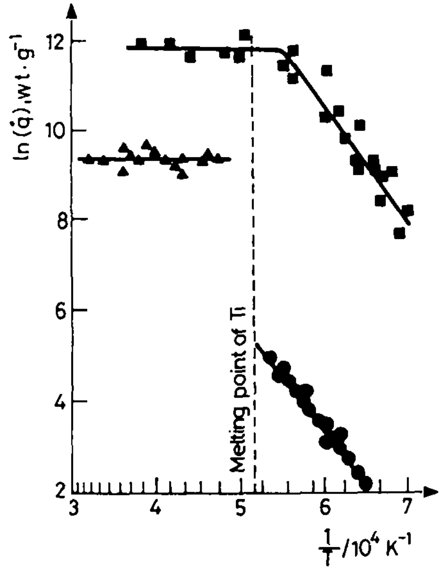

Fig. 3 Temperature dependence of chemical heat release rate during the interaction of titanium with carbon black ■ — and titanium with graphite: ● — former work [6]; ▲ — former work [7]

To study heat evolution accompanying the high-temperature reaction of silicon with carbon, a time dependence of luminance temperature of sample surface at different heating rates was recorded in the course of the ETE development.

Figure 4 gives the Arrhenius representation of rate of chemical heat evolution during reaction of silicon with different dispersions of graphite as a function of temperature, obtained by treatment of ETE curves.

The ETE curves treatment procedure is similar to that used in thermal analysis [3]. From these curves, it is clear that the ETE process in the silicon-carbon system is stepwise in nature. At the initial stage the intensity of chemical heat evolution after melting of silicon depends exponentially on temperature, with the apparent activation energy E equal to 55±4 kcal·mol^{-1} for both mixtures No. 1 and No. 2 (Table 1). At a temperature of about 1930°C the rate of heat evolution reaches its maximum for both graphite dispersions. On heating further the rate of heat evolution decreases. The conclusion to be drawn is that the limiting stage of the process is the liquid-phase diffusion of carbon in silicon, which arises because of differences in carbon concentration in the melt near the surface of carbon particles and near the carbide particles.

Similar experiments were carried out in the tantalum-graphite system. In these experiments, where the temperature distribution in the bulk of the sample was uniform, the rate of chemical heat release was calculated as a function of temperature. This dependence is represented by the Arrhenius plot in Fig. 5 (curve 1). The considerable deviation of the curve from a straight line testifies to strong self-retardation. The apparent activation energy can be calculated from the slope of the linear part of this curve; it was found to be approximately equal to $E_{app} = 140 \pm 40\ 4$ kcal·mol^{-1}, but showed low reproducibility.

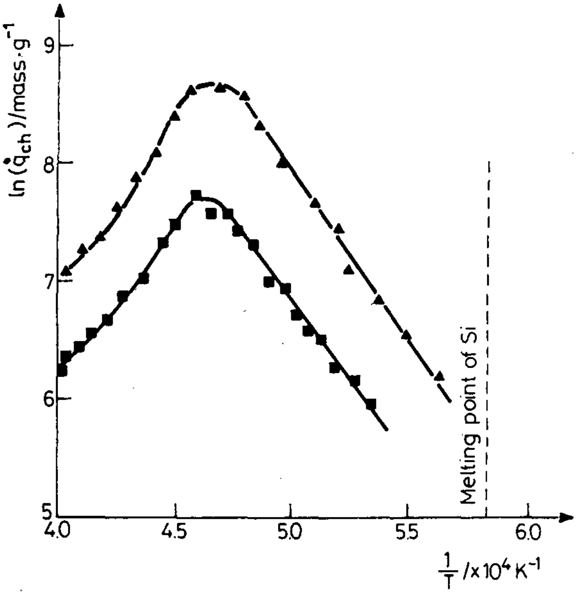

Fig. 4 Temperature dependence of chemical heat evolution during the interaction of silicon with graphite in different dispersions: ▲ — mixture No. 1; ■—mixture No. 2

In addition, experiments were carried out on the system Ta–C with a preliminary treatment of the samples at $T = 1200$ K, $t = 20$ sec, which aimed to prove experimentally the retardation of the interaction in aged samples. However quite opposite results were obtained: the rate of chemical heat release increased by about one order of magnitude (Fig. 5, curve 2). The most likely explanation is that sintering occurring during preliminary heat treatment increases the contact surface of the reactants to accelerate interaction at the thermal explosion step.

Table 1 Mixtures studied

Mixture	Powder dispersions / µm	
	Silicon	Graphite
No. 1	$5 < \delta < 16$	$\delta < 63$
No. 2	—	$63 < \delta < 90$

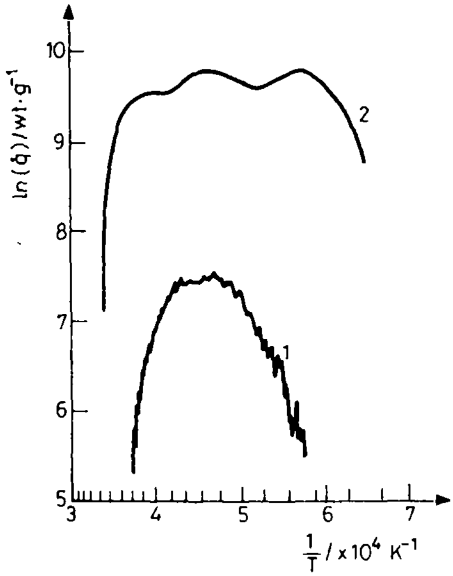

Fig. 5 Temperature dependence of chemical heat release rate during the interaction of tantalum with graphite, 1 — control sample; 2 — thermally treated sample (T = 1200 K, t = 20 sec)

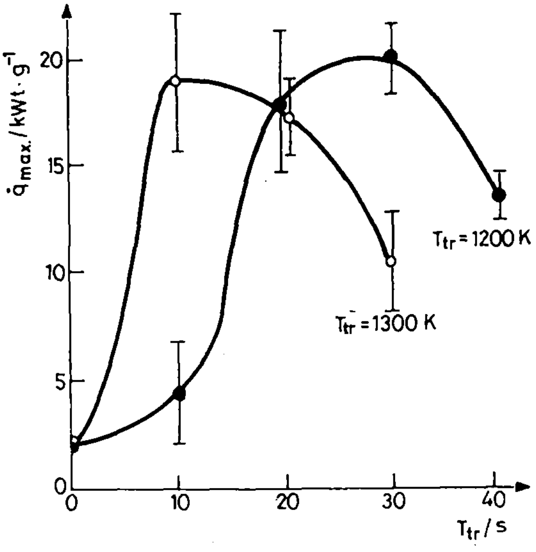

Fig. 6 Dependence of maximum heat release intensity in the Ta–C system at the explosion stage on the pre-heat treatment time

However, some retardation of the interaction in the Ta–C system was observed as a result of pre-heat treatment of samples for long times of heat treatment. The retardation corresponds to the decreasing part of the dependence of maximum heat release during thermal explosion on the pre-heat treatment time, as shown in Fig. 6. Apparently, the interaction retardation, caused by reaction product formation, and the interaction acceleration, caused by partial sintering, occurred simultaneously as a result of pre-heat treatment. When the pre-heat treatment time is not too large, the sintering effect prevails. When the accelerating effect of sintering at its maximum development, the influence of autoretardation becomes noticeable.

Conclusions

In summary, the ETE method makes it possible to study the kinetics of heat release of exothermic reactions in powder mixtures at temperatures reaching the combustion temperatures in these systems. As a consequence conclusions can be drawn on the interaction mechanism in such extreme conditions.

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Zusammenfassung — Unter der Bezeichnung elektrothermische Explosion (ETE) wird eine neue thermoanalytische Methode beschrieben, bei der ein gleichmäßiges Erhitzen der Probe bei äußerst hohen Geschwindigkeiten (bis zu 10^5 deg·s^{-1}) erreicht wird. Das Erhitzen erfolgt im Primärschritt durch einen direkten Stromdurchfluß durch die Probe und nachdem die Zündungsbedingungen erreicht wurden, durch die Reaktionswärme. ETE ist die einzige direkte Methode, die die Untersuchung der Makrokinetik von heterogenen Reaktionen in kondensierten Systemen bei hohen Temperaturen und kurzen Umsatzgeschwindigkeiten erlaubt, was für übliche thermoanalytische Geräte (bis 3500 K und 10^{-2}) unerreichbar ist.

In Anwendung der Methode werden kinetische Daten für Hochtemperatur- und Hochgeschwindigkeitswechselwirkungen in Pulvergemischen von Kohlenstoff mit Titan, Silizium und Tantal dargelegt. Die Geschwindigkeit der Wärmefreisetzung im Ti–C-System hängt, nachdem das Metall geschmolzen

wurde, nur zu einem geringen Teil von der Temperatur ab und wird hauptsächlich durch die Lösungsgeschwindigkeit der Kohlenstoffpartikel bestimmt. Der Mechanismus der Wechselwirkung im Si–C-System ähnelt dem des Ti–C-Systemes, jedoch hat die hohe Lösungsenthalpie von Kohlenstoff in flüssigem Silizium eine Gesamtaktivierungsenergie von E=55 kcal·mol^{-1} zur Folge. Die Synthese von Tantalcarbid aus den Elementen im Temperaturbereich 1500-3000 K erfolgt durch einen Mechanismus der Reaktionsdiffusion und verläuft mit starker Eigenverzögerung.