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Macrokinetics of high-temperature heterogeneous reactions: SHS aspects

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Abstract - High-temperature transformations of matter at the SHS wave is considered. The experimental problems arising in the studies on fast heterogeneous reactions are discussed. Conclusion is drawn that the most informative are here the unconventional nonisothermal methods: electrothermal explosion, electrothermography, DTA and DSC. The results on the high-temperature macrokinetics both in the system 'compacted metal-gas' and in powder mixtures of metals with carbon, boron and aluminum are discussed. Considered is the influence of concomitant processes (sintering, degazing, melting and capillary spreading of one of reactants or eutectics appearing as an intermediate reaction product, etc.). Discussed is correlation between the kinetic and macrokinetic parameters and the regularities of the SHS wave propagation. Outlined are the urgent problems of macrokinetics of high-temperature heterogeneous reactions at the SHS wave.

INTRODUCTION

The self-propagating high-temperature synthesis (SHS) is one of prospective methods for obtaining high-temperature materials and products on their basis. It has some advantages as compared to traditional furnace synthesis: a higher productivity, a lower power consumption, a possibility of combining the synthesis with different physical actions on matter, for example, by pressing a plastic, non-cooled combustion product. To control the synthesis process with purpose of obtaining materials with pre-selected properties one must have information about the mechanism and macrokinetic laws of reactants interaction in the SHS wave.

The SHS is known to be a multi-stage process. In the majority of cases we are dealing with two stages, the first one of which takes place at rather high (though not maximal) temperatures. The kinetics and macrokinetics of processes, corresponding to this stage, stipulate combustion front propagation laws. The second stage - the structure formation stage - develops far enough behind the combustion front. The kinetics of processes at this stage may essentially differ from that of the first stage. Nevertheless, a rather high heat power level is peculiar to this stage as well. Besides, the kinetics and macrokinetics of the second stage have a critical influence on many technological characteristics of the SHS process and on a complex of basic physical, chemical and morphological characteristics of the product obtained. In some cases the stages can more or less merge, but this is the exclusion, rather then the rule. Unfortunately, now we are still exploring the approaches to studying the kinetics of the first stage, though, fortunately, the works have already appeared, which use the synchrotron radiation (that will be considered in more detail below), which helps to investigate the kinetics of phase formation at the second stage as well. In virtue of absolute incommensurability of the quantities of works related to studying the macrokinetics of these two stages, below we shell discuss the first stage mostly.

Since the SHS wave propagation is a rapid high-temperature process, the macrokinetics of appropriate reactions should be investigated at high temperatures. At first sight, they can be investigated at lower temperatures and at longer times by applying classical isothermal approaches of chemical kinetics with subsequent extrapolation of results into the high-temperature region of practical interest. This way is practically inapplicable for studying SHS processes, however. In virtue of high complexity of state diagrams of SHS systems one can not expect that the reaction mechanism and the composition of reaction products will remain unchanged with changing the temperature level.

SHS REACTIONS INVESTIGATION METHODS

The methods used for investigating the kinetics of reactions in condensed systems, developed in the classical chemical kinetics, are inapplicable for studying SHS-reactions at high temperatures in the overwhelming majority of cases. This is both due to principal difficulties of thermostatic processing of samples in the temperature range of practical interest (up to 3000-3500 K) and due to short duration of processes under study (characteristic conversion times may be of the order of 0.1 - 0.01 s and lower). In some cases the important kinetic information can be gained by means of nonisothermal methods of studying the chemical reaction kinetics, which were analyzed and classified by Merzhanov (ref. 1).

The methods based on the experimental determination of combustion regularities have been mostly used for studying SHS-reactions. There are many papers in which the conclusions about the reaction kinetics were drawn based on experimentally obtained dependencies of combustion rate on the initial temperature (ref. 2, 3), or on the degree of system dilution by an inert filler (ref. 4, 5), or on the maximal temperature achieved in a combustion wave (ref. 6, 7). Indeed, such an approach is attractive due to its simplicity and possibility of obtaining information about the processes occurring at extremely high temperatures. These approaches were taken from Zeldovich's theory of combustion (ref. 8) and are finally reduced to the determination of activation energy from the slope of a curve drawn through experimental points at coordinates $\ln(u/T_c) - 1/T_c$, where u is the combustion rate, T_c is the combustion temperature. This approach, however, is correct only if the combustion wave has the so-called narrow reaction zone, i.e. if the chemical heat release occurs mainly in a rather narrow temperature range, whose width is of the order of one Semenov's interval RT_c^2/E near the combustion temperature.

Much more complete information on reaction kinetics in the SHS wave can be obtained by recording the temperature profile in the combustion front (ref. 9, 10). For this purpose one usually applies very thin (of 5 ÷ 7 μm) low-inertion tungsten-rhenium thermocouples, because the temperature growth rate in the combustion front can reach extremely high values, up to $10^5 \div 10^6$ K/s. Sometimes the temperature profile is recorded by pyrometry (ref. 11), that allows to determine the qualitative characteristic of the process only.

Without any doubt, the study of temperature fields of real SHS-compositions always provides very rich information about the qualitative side and, frequently, about the mechanism of chemical processes in the combustion front as well. Thus, one can record the melting of initial components, intermediate or final reaction products. One can also determine the stage character of the process and, in particular, distinguish the propagation stage responsible for combustion rate and the post-combustion stage that was considered above. The results obtained by this method have greatly influenced the modern concepts of combustion mechanisms for many SHS-systems.

Now one should make some remark regarding the kinetic interpretation of SHS wave temperature profiles. If the temperature conductivity at the combustion front does not change, this technique allows to determine the chemical heat release intensity from a temperature profile distortion. If, however, the temperature conductivity at the front drastically changes (what can take place in practice as a result of various physico-chemical processes, such as sintering, phase transformations, etc.), there arises a real danger to take the temperature profile distortion, caused by temperature conductivity changing, for chemical heat release result.

Two more specific techniques were developed for studying the reactions occurring in the gasless combustion wave. In one of these techniques the combustion wave front is freezed (for example, when the system is burning in a wedge-like gap between two copper blocks), after which the structure of interaction products in the extinguishing coordinate vicinity is studied by X-ray microanalysis methods (ref. 12, 13). This approach allows to estimate the length of characteristic stage interaction zones, makes it possible to determine the composition and structure of intermediate products and to investigate physico-chemical features of the transformation.

The method which is especially prospective for studying the gasless combustion wave, is the time-resolved X-ray diffraction (TRXRD) by using an intense source of synchrotron radiation and a position-sensitive photo diode array detector (ref. 14). This method allows to study the phase transformation dynamics in the SHS wave post-combustion zone. For studying the propagation zone this method lacks spatial resolution, however, - the synchrotron radiation beam width is of the order of 1 mm, which is larger than or comparable to the gasless combustion front width.

The macrokinetic regularities of SHS-reactions can also be determined from ignition parameters measured experimentally. In this case one can use the following parameters as basic characteristics: the ignition delay time, the critical values of temperature or of a sample surface heating pulse energy, the density of a thermal flux heating the sample, etc. (ref. 15, 16). Unfortunately, the correct treatment of SHS-systems ignition experiments is rather difficult due to the influence of a complicated transformation law, due to increasing role of radiation heat losses and so on.

The thermoanalytic methods (such as DTA, DTG, DSC and others) allow to get a much more reliable kinetic information as compared to combustion and ignition methods, but these techniques 'work' within the range of temperatures essentially lower than those achieved in the SHS wave. In some cases the temperature range accessible for thermoanalytic experiment can be extended by strong dilution of a reactants with an inert (ref. 17, 18). There exist two methods of dilution: the 'mechanical' dilution (where the composition under study is mixed with a diluter powder) and the 'thermal' dilution (where the composition is clutched as a thin layer between two massive heat-conductive diluter blocks). The 'thermal' dilution has been successfully used for studying the macrokinetics of reactions in heterogeneous SHS-charges (ref. 67).

Among various thermoanalytic methods of studying SHS-reactions one should distinguish the electrothermographical method (ETM) developed in works by Grigor'ev et al. (ref. 19, 20). This method is based on programmed heating by electric current of a thread which is a reactant and a high temperature source simultaneously. The second reactant may be either the gas, in the medium of which the thread is heated (ref. 21), or the substance deposited on a thread surface in advance (ref. 22). The ETM is a high-speed method due to short time of thermal relaxation of a thin thread. The reaction process can be monitored within the ETM framework by chemical heat release intensity and by the thickness of product films generated. Besides, the kinetic parameters in ETM can be determined from thread ignition characteristics (ignition limits, induction periods) by solving a reciprocal problem of the ignition theory. The ETM provides a principal possibility of studying the macrokinetics of heterogeneous reactions just in the same temperature range, where these reactions proceed in the SHS wave. However, the data obtained with ETM have not been widely applied in studying combustion laws. In our opinion, this is mainly due to different reaction properties of a smooth surface of threads and of a highly-defective surface of powder particles used in SHS.

Probably, the method, which is most adequate to studying the SHS-reactions macrokinetics, is the so-called electrothermal explosion (ETE) method - the thermal explosion that occurs when a reaction-capable sample is heated by direct passing the electric current through it (ref. 23, 24). In the ETE process the reaction can occur in the uniform mode over a sample volume, which makes it possible to calculate kinetic parameters quantitatively from experimental thermogrammes. Besides, some essential advantage of this method lies in the process quasiadiabaticity associated with extremely high (up to 10^5 K/s) rates of growth of a sample temperature.

The growth of sample temperature T during ETE in the absence of heat losses is determined by heat release due to chemical reaction $\dot{q}_{ch}$ and by electric heating $\dot{q}_{el}$ (ref. 25):

$$c\rho(dT/dt) = \dot{q}_{ch} + \dot{q}_{el} \tag{1}$$

where c is the heat capacity, ρ is the density, t is the time. In the temperature region, where the chemical power is comparable to or higher than electrical one, $\dot{q}_{ch}$ can be calculated, according to (1), from a current slope of a thermogramme. The calculation of $\dot{q}_{ch}$ is further simplified, if the electric heating is turned off during the explosion.

MACROKINETICS OF SHS-REACTIONS

Macrokinetics of high-temperature synthesis of carbides

Among the SHS-systems the equiatomic powder titanium-carbon mixture is the mostly studied one, which is due to its practical value and also due to the fact that it is suitable as a model for developing the theory of SHS-processes. A typical feature of this system is the fact, that at temperature essentially lower than the combustion temperature one of system's reactants - the titanium - is melted. There are various opinions in the literature regarding the mechanism and kinetics of high-temperature interaction in this system. So in studying the liquid titanium carbonizing in a graphite crucible two interaction stages were observed: 1 - an intense carbon dissolution in a diffusion mode; 2 - upon reaching some particular carbon concentration in a melt the carbide layer was formed at the graphite surface, and the dissolution through this layer was proceeding much slower (ref. 26).

The titanium-carbon system combustion laws were first studied systematically by Shkiro and Borovinskaya (ref. 2). They have obtained experimental dependencies of product composition and combustion rate on a sample diameter and density, on a titanium dispersness, on an initial temperature and on the degree of charge dilution with an inert material - titanium carbide.

In (ref. 27, 28) the titanium - carbon interaction was studied by the TRXRD method with using synchrotron radiation. The first of these papers reported about 5 ÷ 7 s delay in forming the final product phase after the combustion wave propagation. In paper (ref. 28) the delay has also been observed, though not so long: the TiC phase formation was terminated in 0.4 s after titanium melting.

The electron-microscopic investigations, carried out on model samples of particle-film type show that the interaction of carbon with titanium takes place after liquid phase formation only (ref. 29, 30). In this case a primary product layer is formed between reactants, which grows simultaneously from the solid carbon side and then is dissolved in a liquid titanium.

In paper (ref. 31) the macrokinetics of titanium and tantalum interaction with carbon in the SHS process was studied from the admixture gas release from the 'cold' and 'hot' ends of a sample. The gas permeability of combustion products occurred to be higher than that of corresponding initial charges. The conclusion was drawn, that the size of pores increases during combustion and their number lowers. In the titanium-carbon system this effect arises due to formation of large pores at the place of titanium particles which are melted during the combustion and then spread over the soot.

A similar results was obtained in paper (ref. 32), where it was shown experimentally for the first time, that the large titanium particle pressed into the Ti-C charge is melted during the combustion and spreads over the soot, and the hollow sphere remains at its place. In paper (ref. 33) it was found that, depending on titanium dispersness, the process rate may be limited by either reaction kinetics or capillary spreading. This conclusion was confirmed experimentally.

Vadchenko et al. (ref. 34) in their paper, devoted to the interaction of titanium and zirconium threads with soot coating, first came to a conclusion that the Ti-C system ignition occurs during titanium melting. A quite different conclusion was drawn by Zenin et al. (ref. 35) on the basis of processing the combustion wave temperature profile in the Ti-C system. The authors state that the maximum intensity of chemical heat release is achieved in this mixture at temperature of the order of 1000°C, i.e. long before the titanium melting.

Another opinion was advanced by Doronin (ref. 12). Based on studying concentration profiles of titanium and carbon in a frozen combustion front in this system, the author draws a conclusion, that it is the gas phase that plays important role in occurring of this reaction. The studies with SHS front freezing, carried out in (ref. 36), have shown that the reaction in the Ti-C system begins to proceed at a noticeable rate after titanium melting and the primary product is formed in the melt bulk.

In works of authors of this review the titanium-carbon interaction was studied by the ETE method. The titanium-graphite mixture was found to be ignited during titanium melting and the titanium-soot mixture - at much lower temperatures. Fig. 1 shows in the Arrhenius representation the data on a temperature dependence of chemical heat release intensity in titanium-graphite and titanium-soot systems (ref. 37). Before titanium melting the reaction rate strongly depends on temperature - the activation energy is E=50 kcal/mole. After titanium melting the reaction is thermally non-activated and occurs according to the pseudo-zero law. The conclusion was drawn, that after titanium melting the reaction is limited by the diffusion process - the carbon dissolution in a liquid titanium. In this case one can explain both the process non-activation (the activation energy of a liquid-phase diffusion is close to zero), and the pseudo-zero transformation law. One can easily show that the formal transformation law corresponding to particle dissolution has the form $\varphi(\eta)=(1-\eta)^{1/3}$, which is quite close to zero law within a wide range of variation of transformation depth η.

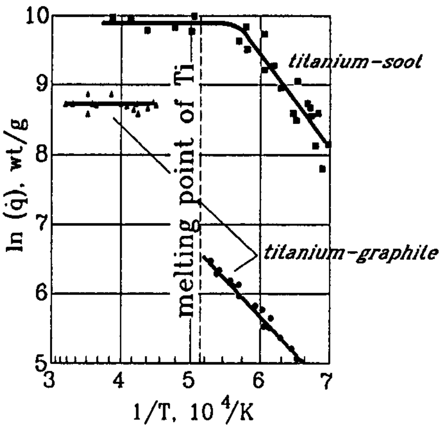

Fig. 1. Temperature dependence of chemical heat release intencity in titanium-carbon system (ref. 37).

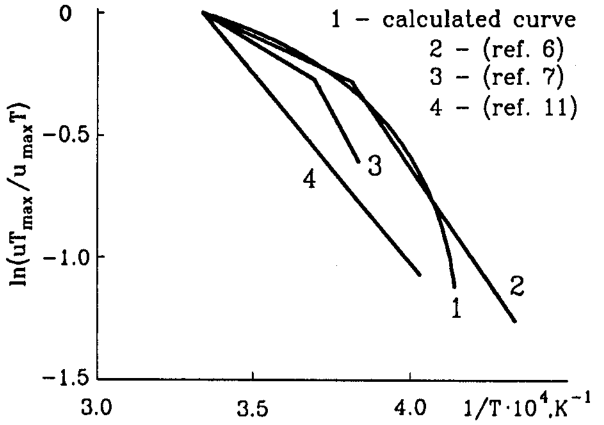

Fig.2. The approximation of the experimental data on combustion rate in Ti-C system (ref. 6, 7, 11) by a curve, calculated from the Daniell's theory.

The results obtained allowed to make a conclusion about the mechanism of the Ti-C system combustion. The steep Arrhenius dependence of chemical heat release intensity on the temperature up to the titanium melting point allows to approximate the heat release function $\dot{q}(T)$ by a step:

$$\begin{array}{ll} T_0 < T < T_* & \dot{q} = 0 \\ T_* < T < T_m & \dot{q} = \dot{q}_{max} = \text{const} \end{array} \qquad (2)$$

where T_* is the titanium melting point, T_m is some temperature, close to maximal one, at which the carbon dissolution in titanium practically ceases[1]. In this case the combustion rat u is described by Daniell formulae (ref. 38) which have been suggested as early as in the 'pre-Zeldovich' epoch:

$$\begin{array}{l} (T_* - T_0) / (T_m - T_0) = (1 - \exp(-\xi)) / \xi \\ u^2 = \xi \cdot a \cdot \dot{q}_{max} / c\,(T_m - T_0) \end{array} \qquad (3)$$

where ξ is the parameter, $a=\lambda/c\rho$ is the temperature conductivity. From this point of view it is of interest to look at the results obtained by different authors in the Ti-C system combustion experiments (ref. 6, 7, 11). The temperature dependence of combustion rate is

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[1] This occurs at the moment, when the titanium is exhausted in the system. The non-reacted carbon can still remain in this case, since TiC possesses a wide homogenity region, and the composition of carbide, formed before this moment, can be not strictly stoichiometric one. Thus, the final stage of the reaction proceeds relatively slow in the solid phase and does not already have any influence on the combustion rate.

usually presented in the Arrhenius coordinates, and the activation energy is determined from the slope of the plot. As noted above, a similar procedure of processing the results is correct only if the combustion wave has a narrow reaction zone and if the reaction rate depends on temperature according to the Arrhenius law. This is not the case here. The experimental data should be approximated by a curve calculated from the Daniell theory (Fig. 2). This can be done by selecting a proper discrepancy between combustion temperature measured in the experiment and temperature T_m substituted into the Daniell formulae.

The tantalum-carbon system is far less studied as compared to the titanium-carbon one, but it is also of great interest, because all reactions in this system combustion take place in a solid phase, according to many investigators. The only exclusion is paper (ref. 39.), which states that the intensive interaction in the Ta-C system, as well as in Ti-C, begins only when the liquid phase appears. The electron-microscopic studies, carried out in that paper, have shown that the solid carbide layer of thickness about 0.1 μm is formed between the carbon and liquid eutectic layer. Unfortunately, the temperature has not been recorded in these experiments, which makes it difficult to treat the results of paper (ref. 39) and to compare them with the other authors' data.

The Ta-C system combustion laws were studied in papers (ref. 3, 40). These studies have been carried out at various values of argon pressure, initial temperature, diameter and density of samples. Besides, the tantalum dispersness, the ratio of initial components and the degree of charge dilution with an inert reaction product have been varied. The combustion rate was determined by means of a photoregister. The combustion products were studied by chemical and X-ray-phase analysis methods. A considerable difference in temperature coefficients of combustion rate in dilution ($1.1\cdot10^{-3}$ 1/K) and in the initial temperature ($5.5\cdot10^{-3}$ 1/K), as well as considerable conversion incompleteness, allowed to conclude that the tantalum-carbon system burns with a 'wide reaction zone' (ref. 41, 42). This agrees with the ideas of reaction diffusion as a mechanism of the given reaction.

The growth of product films between tantalum and carbon at temperatures up to 3000 K was studied in (ref. 43). A parabolic law of a product layer growth rate was obtained there. The interaction of tantalum thread with surrounding CO was investigated in paper (ref. 44). It was found, that in this case the Ta_2C film grows at first, and then TaC does. The growth of films obeys the parabolic law. The kinetic constant was obtained for the total film thickness, namely, $k = 99.4 \exp(-49500/RT)\cdot p_{CO}^{1/2}$ $\mu m^2/s$.

Our studies of high-temperature tantalum-carbon interaction, carried out by the ETE method (ref. 45), confirmed this reaction to proceed with a strong autoretardation. At the same time, a preliminary thermal processing of samples in some particular regimes results in a considerable acceleration, rather than deceleration, of interaction at the explosion stage. This effect is caused; apparently, by partial sintering of system components during thermal processing, which leads to increasing the reaction surface. The conclusion was drawn, that the interaction deceleration, caused by reaction product formation, and the interaction acceleration, caused by sintering, occurred simultaneously as a result of preliminary thermal processing. When the thermal processing time is not too large, the sintering effect prevails. When the accelerating effect of sintering is 'limited off', the influence of autoretardation, that is traditional for reaction diffusion, becomes dominating.

Unlike the systems considered above, the reaction in powder silicon-carbon mixture does not occur in the combustion synthesis mode at initial room temperature due to insufficiently high thermal effect value - 16.5 kcal/mole (ref. 46). This reaction can be accomplished, however, in the thermal explosion mode (ref. 47) or with reaction mixture heating by direct passing electric current through it (ref. 48).

In paper (ref. 49) the interaction of liquid silicon with carbon filaments was studied near the silicon melting point by the DTA method. The efficient kinetic constants were determined in the temperature range of 1695 to 1709 K: E = 56.2 kcal/mole, $k_0 = 2\ 10^{11}$ 1/s. The obtained experimental data could not be explained based on the model by Brantov et al. (ref. 50), according to which a limiting stage is the carbon diffusion through the SiC layer. The mechanism of successive endothermal solution of carbon - exothermal precipitation of silicon carbide and related temperature oscillation, - was suggested by these authors.

Similar conclusions were drawn in (ref. 51) based on studying the heat release kinetics in the Si-C system by the ETE method. The process activation energy in the temperature range of 1800 - 2200 K was found to be E = 56 kcal/mole, that is rather close to the enthalpy of carbon solution in liquid silicon ΔH = 55 kcal/mole (ref. 52). As a result, the following reaction mechanism was proposed: the carbon particles are dissolving and the carbide particles are growing simultaneously in a liquid silicon. The carbon concentration in silicon near the surface of carbon and carbide particles grow with temperature according to the same law, but they differ in magnitude. The process is limited by a liquid phase carbon diffusion in silicon.

Macrokinetics of high-temperature synthesis of borides

The titanium-boron system is the most studied one among boride SHS- systems. So, in paper (ref. 53) the temperature profiles of combustion wave in the Ti-αB mixture were recorded by the pyrometric technique (Fig. 3). At some α values the isothermal sections - the titanium and boron melting sites - have been observed on temperature profiles. For α=1 and α=2 these sites are absent, and from the dependence of combustion rate on the temperature, varied by system diluting with an inert, the values of activation energies were calculated, namely, E=55 kcal/mole (α=1) and E=72 kcal/mole (α=2).

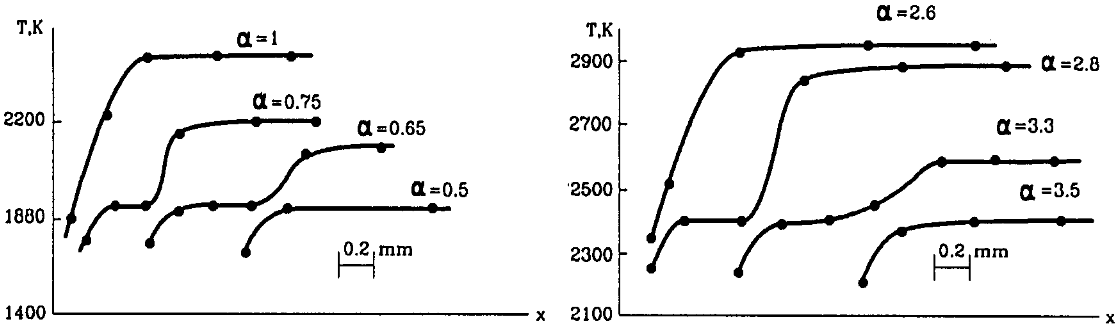

Fig. 3. Temperature profiles of combustion wave in the Ti-αB system (ref. 53).

In paper by Borovinskaya et al. (ref. 54) also from the temperature dependence of combustion rate the following activation energies were determined: $Ti+2B \rightarrow TiB_2$ E=76 kcal/mole, $Zr+2B \rightarrow ZrB_2$ E=74 kcal/mole, $Hf+2B \rightarrow HfB_2$ E=95 kcal/mole. In paper (ref. 55) the kinetic parameters of interaction of transition metals with boron were determined by processing the temperature profile of combustion wave recorded by means of a thermocouple. The heat release function was sought in the form: $Qk_0\exp(-m_0\eta-E/RT)$ (Table 1).

TABLE 1. Kinetic parameters of interaction of transition metals with boron (ref. 55)

System	Qk_0, cal/cm^3/s	m_0	E, kcal/mole	interval of η
Nb+2B	6.6 10^7	12±0.2	35±5	0.4 ÷ 0.9
Nb+B	2.4 10^{12}	23±1	50±10	0.4 ÷ 0.8
Ta+2B	8.8 10^{11}	18±1	50±10	0.4 ÷ 0.9
Zr+2B	1.2 10^8	10±0.2	34±4	0.3 ÷ 0.9
Hf+2B	9.7 10^9	15	40±5	0.5 ÷ 0.9

The study of the titanium-boron system by the ETE method (ref. 56) has shown that this reaction begins to proceed at a noticeable rate long before the titanium melting. Besides, it occurred that, as it took place for the tantalum-carbon system, some initial interaction stage (probably, the reactants sintering) accelerates the process. This was manifested in an anomalous, falling dependence of maximal chemical heat release intensity at the explosion stage on the electric power, i.e. the slower the sample is heated (and, accordingly, the longer it occurs to be kept at high temperature before explosion), the higher the maximal reaction rate in the run.

Macrokinetics of high-temperature synthesis of intermetallides

The laws of gasless combustion of mixtures of metal powders were investigated in papers by Naiborodenko and Itin (ref. 4). The activation energy of components interaction was determined from the temperature dependence of combustion rate. In the Co-Al system the activation energy was found to be 32 kcal/mole, and in the Ni-Al system, for high charge dilutions with an inert, - 33 kcal/mole, and for low ones - 18 kcal/mole. The latter figure well agrees with the activation energy of diffusion nickel solution in an aluminum melt, that was obtained by equally-accessible method, namely, 18±3 kcal/mole.

In papers (ref. 57, 67) the regularities of exothermal interaction in binary mixtures of aluminum with transition metals - nickel, titanium, zirconium and cobalt - were studied by DTA method - with and without thermal dilution. It was found that, depending on temperature, the interaction of aluminum with metals mentioned occurs in one of two qualitatively different modes. The solid-phase interaction in the Ti-Al and Zr-Al systems takes place at temperature lower than the aluminum melting point and in the Ni-Al and Co-Al systems - at temperatures lower than melting points of corresponding eutectics. The effective activation energies of solid-phase reactions were determined to be equal to: E_{Ni+Al} - 37 kcal/mole, E_{Ti+Al}; - 60 kcal/mole, E_{Co+Al} - 32 kcal/mole, E_{Zr+Al} - 24 kcal/mole. The critical thermal explosion conditions in mixtures under consideration were found to be associated with the solid-phase interaction kinetics. Under the experimental conditions the classical thermal explosion took place, however, in the Ni-Al system only. In other mixtures the thermal explosion occurred before reaching critical conditions corresponding to the solid-phase reaction kinetics. This effect was caused by a sharp growth of heat release intensity as a result of jump-wise increasing of the contact surface of reactants due to capillary spreading of liquid eutectics generated.

Based on above experiments, as well as on the data of X-ray and metallographic studies, the authors of (ref. 67) have proposed the following scheme of stage development of the high-temperature interaction process in the nickel-aluminum system:

$$\mathrm{Ni+AL} \xrightarrow{k_1} \mathrm{NiAl_3} + 258\ \mathrm{kcal/mole} \tag{4}$$

$$\mathrm{Ni + NiAl_3} \xrightarrow{k_2} \mathrm{Ni_2Al_3} + 90\ \mathrm{kcal/mole} \tag{5}$$

$$\mathrm{Ni + Ni_2Al_3} \xrightarrow{k_3} \mathrm{NiAl} + 212\ \mathrm{kcal/mole} \tag{6}$$

Even at T = 550°C reaction (5) occurs at rates commensurable with the rates of process (4) and, as the temperature grows up to 640°C (the melting point of the Al-$NiAl_3$ eutectic (ref. 68)) and higher, $k_2 > k_1$ and the proceeding of (5) is limited by rate k_1. The validity of this scheme is confirmed by metallographic investigations by Naiborodenko and Itin et al. (ref. 69). These investigations have shown that after annealing in the Ni-Al bi-metal at 560°C two phases are present, one of which is identified as Ni_2Al_3, and the second one is, apparently, $NiAl_3$. As the temperature grows up to 620°C, only Ni_2Al_3 phase remains, i.e. constant k_2 became higher than k_1.

In paper (ref. 58) the nickel-aluminum interaction has also been studied by the thermoanalytical method. The first peak corresponds to a purely solid-phase interaction. At relatively high sample heating rates only one peak was observed, and the reaction was occurring with the liquid phase participation.

Macrokinetics of high-temperature synthesis of nitrides

Kinetic laws of the interaction of transition metals with nitrogen have been systematically studied by the electrothermographical method in papers by Vadchenko and Grigor'yev et al. (ref. 59, 60). The sought constants were determined from the rate of growth of a product film on the surface of a metal wire immersed in nitrogen and heated by passing electric current. Some of results obtained are presented in Table 2.

In Aldushin's paper (ref. 61) kinetic constants of tantalum-nitrogen interaction were used for theoretical calculation of combustion rate in this system. The value u=2.5 cm/s, obtained by the author of (ref. 61), was in a good agreement with experimentally measured rate of tantalum combustion in nitrogen, that is equal to 2 cm/s (ref. 62).

TABLE 2. Kinetic constants of the interaction of transition metals with nitrogen (ref. 60)

Metal	T, °C	Resulting phase	$k_1=k_{01}\exp(E/RT)$, cm^2/s			
			k_{01}	k_{02}	E_1, kcal/mole	E_2, kcal/mole
Ti	1300-1600	Solid solution in α-Ti	$2.6\cdot10^{-3}$	$6.5\cdot10^{-3}$	37.4	40
Zr	1550-1830	Solid solution in α-Zr, ZrN_{1-x}	0.525	$4.4\cdot10^{-2}$	37.4	51.6
Nb	2050-2250	NbN	7.6	$2.3\cdot10^{4}$	87	124
	2250-2450	NbN	$8.5\cdot10^{-2}$	$2.2\cdot10^{6}$	110	146
Ta	2490-2930	TaN	0.21	0.3	77.6	75.4

Borovinskaya in her paper (ref. 63) supposed that the SHS wave can propagate due to the heat released during non-metal dissolution in a metal. Here it was noted that the combustion of transition metals in nitrogen may be followed by the formation of an oversatureted phase of a final product. The combustion rate is not influenced by this decay already.

THE MECHANISM OF SHS-REACTIONS

Extremely high temperatures - 2000 to 3500 K - are reached in the course of SHS as a result of occurring high-exothermal reactions. In the majority of cases the maximum temperature of the SHS wave exceeds the melting point of one of reactants at least. In this connection the question arises: in which phase does proceed the limiting stage of reaction in the combustion wave propagation zone? This question is rather complicated, and often one can encounter in the literature diametrically opposite opinions even about the same system.

From this point of view, the following interesting fact should be noted, which, apparently, has been ignored so far. The combustion rates of many SHS-systems lie within a relatively narrow interval - from some millimeters per second up to some centimeters per second (ref. 64). Naturally, one can conclude that the rates of limiting stages of various SHS-reactions also differ not so much. This favors indirectly two possible mechanisms of SHS-reactions in systems, where the liquid phase can be formed in the combustion front:

1 - the limiting stage of interaction is the diffusion in a liquid phase. As known from the kinetic theory (ref. 65), the coefficient of diffusion in liquid is mainly determined by the collision cross-section of molecules, it weakly depends on temperature and is usually equal to the same value for quite different systems - the value of the order of $10^{-5} cm^2/s$.

2 - the limiting stage of reaction is a solid-phase diffusion at temperature close to a melting point of a more fusible reactant. As a confirmation of the possibility of this version, Fig. 4 presents in traditional coordinates temperature dependencies of solid-phase diffusion coefficients of carbon in some transition metals, It is seen that

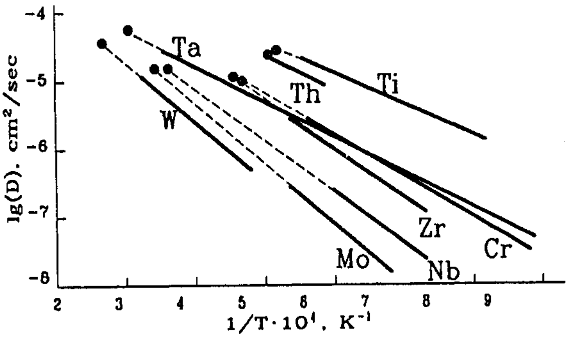

Fig. 4. The dependence of solid-phase diffusion coefficients of carbon in transition metals on temperature.

at a melting temperature of corresponding metal the solid-phase diffusion coefficient also reaches the level of a coefficient of diffusion in liquid, namely, 10^{-5} cm^2/s. As it was shown above for the example of Ti-C system, in the case, when the reaction in the SHS propagation zone is limited by a liquid-phase diffusion, the rate of interaction after liquid phase formation is nearly constant, and the combustion wave propagation zone width corresponds to the interval from the melting temperature of a more fusible component up to combustion temperature (or, at least, up to some temperature close to maximal one) (ref. 37). For calculating the combustion rate in this case one can make use of the Daniell theory (ref. 38) that is based on the supposition about reaction rate constancy within the range from the ignition temperature up to combustion one.

The gasless combustion in the case, when the reaction is limited by a solid-phase diffusion at temperature close to the melting point, was considered in paper (ref. 66) and it was called the elementary combustion model of the second kind. In this case it was assumed that the melting zone with constant temperature is formed in the combustion wave, and this zone screens the action of more high-temperature wave sections on the initial mixture.

One more combustion model, which is important for condensed systems (the so-called wide reaction zone model), corresponds to the exothermal reaction occurring with strong autoretardation (for example, with parabolic or exponential transformation law) (ref. 41, 42). The systems, which can burn in such a manner, are, for example, those ones, in which the melting temperature of initial reactants, as well as of intermediate and final products, is higher than corresponding temperatures in zones, where these substances are present or formed. The chemical interaction of reactants in these mixtures takes place in a solid phase according to the reaction diffusion mechanism. In the 'wide zone' model the combustion rate is determined by some intermediate temperature at which the reaction rate reaches a maximum, rather than by maximal combustion temperature.

In conclusion, we would like to mention, that the mechanism and kinetics of SHS-reactions, as well as the combustion wave propagation rate, may depend on many physico-chemical features of a reacting mixture in any particular case. Of great significance here may be the dispersness and morphology of initial powders, the homogeneity of their mixture, the mixture porosity, the presence of chemical admixtures and adsorbed gases in reactants. All these factors, along with the limitation of experimental means for studying the reactions at extremely high temperature and short times, makes the problem under consideration extremely complicated. Nevertheless, the importance of information about the mechanism and macrokinetic regularities of reactants interaction in the SHS wave for synthesis of materials with required properties has stimulated, both before and in recent years especially, great efforts of many investigators in this direction.

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