

## CHEMICAL ACTIVATION OF THE SHS PROCESS IN THE Nb-C SYSTEM

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*The phenomenon of chemical activation is investigated using combustion of the Nb—C system in the presence of an activating additive, namely, polytetrafluoroethylene, as an example. Regions of the parameters of the process are found where the interaction occurs by two different mechanisms. The characteristic features of the process are established and the role of the activating additive in each region is determined.*

In the problem of SHS much attention is presently given to the issues of chemical activation of the combustion processes [1, 2]. Hydrocarbon (including halogen-containing) polymers, gasified in SHS, are commonly used as activators of combustion of carbon-containing systems. Introducing similar additives makes it possible, apart from intensification of combustion, to obtain valuable information on the role of gas phase mass transfer in the mechanism of SHS processes.

The present work gives the results of the experimental investigation of the laws of combustion of the Nb—C system in the presence of polytetrafluoroethylene additives. The choice of this system as an object of investigation is governed by the fact that it falls in the category of "difficulty burning": the SHS process is possible only when a finely dispersed niobium powder ( $r < 15 \mu\text{m}$ ) is used and the specimen is pressed down [3]. In addition, the mechanism of combustion and phase formation of Nb—C is virtually not studied.

The experiments were carried out in a constant-pressure bomb by a known procedure on specimens with  $d = 20$  and  $30 \text{ mm}$  and  $\Delta = 0.6-0.65$  in an argon atmosphere at a pressure of  $0.5-50 \text{ atm}$  with polytetrafluoroethylene contents of  $0.1-5.0 \text{ wt. \%}$ . Niobium powders with  $r < 15$ ,  $r < 40$ , and  $r < 50 \mu\text{m}$  and of the fraction  $63 < r < 71$ , lampblack with  $r < 1 \mu\text{m}$ , and powdered polytetrafluoroethylene with  $r < 10 \mu\text{m}$  were investigated. The maximum combustion temperatures were measured by a tungsten-rhenium thermocouple with  $d = 0.1 \text{ mm}$ . The mean values of the burning rates were determined from signals of several thermocouples sealed into the specimen at a specified distance from each other. In a number of cases special markers, namely, strips of niobium foil  $100 \mu\text{m}$  thick and  $1.0-1.5 \text{ mm}$  wide, were pressed into the tablets. The burnt specimens were subjected to chemical and X-ray phase analysis on a DRON-0.5 diffractometer. The product and marker microstructures were investigated on a BS-300 scanning electron microscope.

The experiments were carried out on the stoichiometric mixtures  $\text{Nb} + \alpha\text{C} + \beta\text{C}(-\text{C}_2\text{F}_4-)_n$  with  $\alpha + \beta = 1$ , where  $\alpha = C_e/\text{Nb}$ ,  $\beta = C_f/\text{Nb}$  are the stoichiometric coefficients;  $C_f$  is the amount of carbon which is to be formed with complete decomposition of a given amount of polytetrafluoroethylene.

Preliminary experiments showed that the minimum value of the additive content, with which the system gains the capacity to burn, corresponds to  $\beta = 0.003$ . The data of [3] are simultaneously confirmed: it is shown that in the absence of the additive the Nb—C system burns only when  $r < 15 \mu\text{m}$  and the specimen is pressed down; in this case  $T_c = 2600^\circ\text{C}$ ,  $U_b = 2.5 \text{ mm/sec}$ .

The investigations were subsequently performed in the direction of studying the characteristics of combustion ( $T_c$ ,  $U_b$ ,  $\varepsilon$ ) and the chemical and phase composition of the products as functions of the basic parameters of the process ( $\beta$ ,  $P_{\text{Ar}}$ ,  $r_{\text{Nb}}$ ). From Fig. 1, which gives  $T_c$  and  $U_b$  as functions of  $\beta$ , it follows that for each value of  $P_{\text{Ar}}$  there is a minimum value  $\beta'$ , below which the mixtures do not burn. When  $\beta = \beta'$   $T_c$  and  $U_b$  are substantially lower than those for Nb—C with no additives; in this case significant undercombustion and a nonsingle-phase

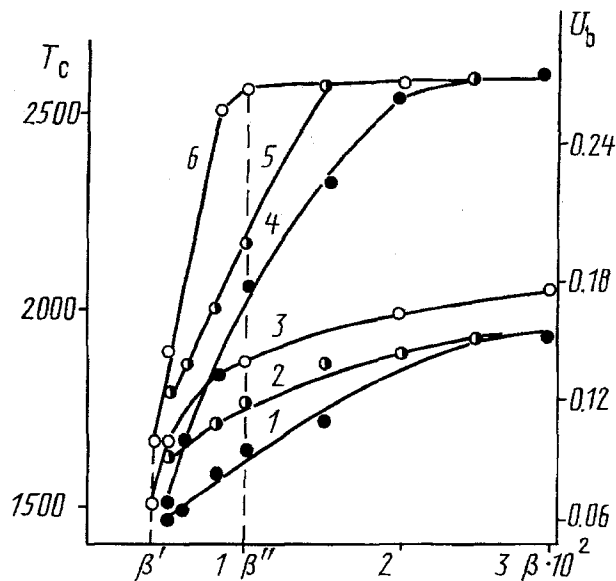


Fig. 1. Burning rate (curves 1-3) and combustion temperature (curves 4-6) vs additive content with  $r < 50 \mu\text{m}$ : 1, 4)  $P_{Ar} = 4$  atm; 2, 5)  $P_{Ar} = 5$  atm; 3, 6)  $P_{Ar} = 10$  atm.  $T_c$ ,  $^{\circ}\text{C}$ ;  $U_b$ , cm/sec.

nature of the combustion product occur. In the interval  $\beta' < \beta < \beta''$   $T_c$  increases sharply and  $\varepsilon$  decreases. With  $\beta \geq \beta''$   $T_c$  remains constant, the combustion product contains single-phase NbC with a  $C_{fr}$  content  $\leq 0.8$  wt. %. The influence of  $\beta$  on  $U_b$  is expressed more weakly and shows up in a monotonic growth of  $U_b$  with increasing  $\beta$  over the entire interval of its values. An increase in  $P_{Ar}$  and a decrease in  $r_{Nb}$  lead to decreasing  $\beta'$  and  $\beta''$  with their simultaneous convergence.

For the convenience of the subsequent discussion the experimental results on  $T_c$  and the phase composition of the products as functions of  $\beta$  and  $P_{Ar}$  are combined in Fig. 2 in the form of a  $\beta - P_{Ar}$  diagram, on which three characteristic regions stand out. In region 0 the mixtures do not burn. In region I the process is characterized by low values of  $T_c$  and  $U_b$  and their growth with both increasing  $\beta$  and  $P_{Ar}$ , the nonsingle-phase nature of the product, and large  $\varepsilon$ . Since in region I  $T_c < T_{m Nb}$  ( $2470^{\circ}\text{C}$  [4]) it is clear that here a mechanism of combustion is realized that is different from the case of the binary Nb—C system, where  $T_c > T_{m Nb}$ . It is obvious that here the interaction occurs when the gas phase participates directly, which agrees with the presence of a strong dependence of  $T_c$  and  $U_b$  on  $P_{Ar}$ . One of the possible ways of such an interaction is the formation (due to the reaction of polymer destruction products with niobium) of highly volatile metal fluorides which perform the gas-transport transfer of the metal to the carbon black surface. The presence of considerable amounts of  $\text{NbF}_3$  in a deposit detected on the bomb walls favors this assumption. Adding carbon in the form of polymer destruction products to the surface of Nb particles may serve as another way. The effectiveness of this mechanism is evidenced by the fact that the metal particles and the niobium markers retain their initial form and size, and growth of the product layers is observed along their perimeter. In region II the SHS process is characterized by  $T_c > T_{m Nb}$  and the eutectic ( $2350^{\circ}\text{C}$  [6]), the product microstructure has a form characteristic of melt crystallization, and the niobium markers lose their form and completely grow together with the specimen material. This fact as well as  $T_c$  close to the  $T_c$  of the Nb—C binary system for the case  $r < 15 \mu\text{m}$  and the character of the dependences studied (constant  $T_c$  and  $U_b$  with growing  $P_{Ar}$ , weak growth of  $U_b$  at  $T_c = \text{const}$  with growing  $\beta$ ) lead to the conclusion that in region II the reactions involving the gas phase play no substantial part and the major contribution to the process of combustion is made by the interaction of the melted Nb with C. It is of importance to note that as  $r_{Nb}$  decreases, regions 0 and I become narrower and with  $r_{Nb} < 15 \mu\text{m}$  they are practically absent, and as  $r_{Nb}$  increases, region I expands at the expense of region II, and already with  $63 < r < 71$  region II no longer exists.

On the basis of the analysis performed it is possible to make some assumptions regarding the mechanism of chemical activation for the combustion process of the Nb—C system. An activating additive plays a dual role in

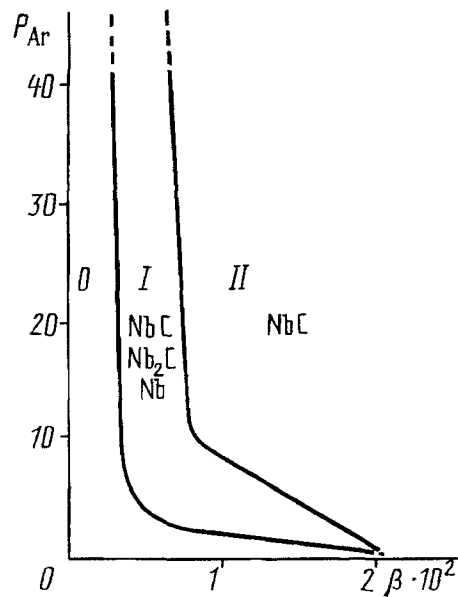


Fig. 2. Diagram of additive amounts - argon pressure;  $r < 50 \mu\text{m}$ ; 0) mixtures do not burn; I) low-temperature region; II) high-temperature region.  $P_{\text{Ar}}$ , atm.

this process. On the one hand, it increases the energy resources of the reacting system (which, however, is not its basic function), and, on the other hand, being the source of highly volatile intermediate compounds, it ensures gas-transport mass transfer, thus decreasing the existing kinetic difficulties. The contribution of the activating additive as a supplier of gaseous carriers of mass shows up most clearly with small  $\beta$  (the low-temperature region I), when by virtue of relatively low temperatures of the process other channels of interaction are practically excluded. With increase in  $\beta$  due to intensification of mass transfer and increase in the completeness of transformation the  $T_c$  grow and, with certain values of the parameters, attain the temperatures of appearance of a liquid phase. In this case the character and the laws of the process are limited predominantly by the reaction  $\text{Nb}_l + \text{C}$  or  $(\text{Nb} + \text{NbC})_l + \text{C}$ ; product formation occurs by melt crystallization. In other words, in the high-temperature region II the importance of the activating additive reduces to the role of "kinetic seed," stimulating the process at relatively low temperatures, as a result of which  $T_c > T_{\text{m Nb}}$  develop and the process proceeds further by the liquid+solid mechanism, which is similar to the case of combustion of finely dispersed niobium with carbon black without an additive.

In summary the following conclusions can be drawn.

1. It is shown that the presence of insignificant (up to 1.0 wt. %) amounts of polytetrafluoroethylene activates the process of combustion in the Nb—C system: the SHS process occurs without any limits.
2. Regions of the parameters of the process are detected where the interaction occurs by two different mechanisms: in the first case (the low-temperature region) the interaction occurs by way of gas phase transport of reagents, in the second case (the high-temperature region) it occurs due to the interaction of the liquid phase (metal or eutectic) with carbon black.
3. The role of an activating additive in the realization of different mechanisms of combustion is identified: in the first case (the low-temperature region) as a basic supplier of gaseous carriers of mass and in the second case (the high-temperature regime) as a "kinetic seed," stimulating combustion in the initial stages of the process.

## NOTATION

$T_c$ , combustion temperature,  $^{\circ}\text{C}$ ;  $U_b$ , burning rate, cm/sec;  $d$ , tablet diameter, mm;  $\Delta$ , relative density of the specimen;  $r_{\text{Nb}}$ , size of the niobium particles,  $\mu\text{m}$ ;  $\alpha$ ,  $\beta$ , stoichiometric coefficients;  $\varepsilon = C_{\text{fr}}/C_{\text{tot}}$ , degree of undercombustion.

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