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INTERACTION OF Zr + Nb WITH CARBON, NITROGEN, AND HYDROGEN IN THE COMBUSTION MODE

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Systematic investigations of combustion of heterogeneous systems based on zirconium, niobium, and nonmetals, viz., carbon, nitrogen, and hydrogen, are conducted. The combustion regularities of three-, four-, and five-component systems and the dependences of the combustion temperatures and rates and the chemical composition of the final products on the process parameters are studied. Changes in the gasless and filtration modes of combustion in multicomponent systems are revealed. The basic factor influencing the formation of single-phase multicomponent compounds are ascertained. Concentration triangles are constructed, which are pseudophase diagrams of the Zr-Nb-C system for combustion in argon, nitrogen, hydrogen, and a nitrogen-hydrogen mixture that represent the evolution of the phase composition of the combustion products, depending on the reaction medium.

Introduction. In recent years, in studying SHS processes a good deal of attention was given to complex systems because, on the one hand, new regularities of the combustion process manifest themselves more abundantly and diversely in them, and, on the other hand, materials with extremal properties can be obtained. Investigations of SHS processes in the Zr-Nb-C-N-H system, reported in the present study, permit competitive parallel and sequential reactions, combining various modes inherent in this system, to be revealed over a wide range of reagent ratios. Such an approach makes it possible, by controlling the combustion, to direct it toward the formation of products of preset chemical and phase compositions. Because of simultaneous effects of different elements, the incorporation phases produced acquire a complex of practically important physicomechanical properties motivating their utilization in modern materials science.

Experimental Part. For ascertaining the effect of each component of the complex Zr-Nb-C-N-H system on combustion, experiments were performed by the following procedure. In each experimental run, the ratio of metals was varied within xZr + (1-x)Nb, where $0.1 \le x \le 0.9$ (at. frac.), and the carbon content was varied within $0.3 \le y \le 9$. Here, the combustion of one and the same composition was studied in an argon atmosphere, then in a nitrogen atmosphere, and finally in a mixture of nitrogen and hydrogen gases with the ratio of partial pressures $1 \le P_{N_2}/P_{H_2} \le 2$.

The basic combustion regularities, namely, the dependence of the combustion temperatures and rates and of the nitrogen and hydrogen content on the Zr/Nb ratios and the pressures of the reacting gases, were studied for the following systems: Zr-Nb-C, Zr-Nb-C-H, Zr-Nb-N, Zr-Nb-N-H, Zr-Nb-C-N, and Zr-Nb-C-N-H (see Table 1).

As a result of the investigations it was found that Nb, while participating in the combustion reactions as a diluent, decreases T_c and u_c at initial stages of the process and affects the formation of complex incorporation phases by stabilizing fcc hydridonitride and carbohydride phases and hindering the formation of hcp hydridonitride and carbohydraide phases.

The effect of zirconium on combustion and phase formation is opposite to the effect of niobium in some cases. Thus, for instance, an increase in the Zr content promotes the formation of solid N_2 solutions in Zr and of hcp hydridonitrides, an increase in the hydrogen content in them, and a rise in the combustion temperatures and rates.

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TABLE 1. Characteristics of Some Single-Phase Compounds

Compound	C	N_2	H_2	a, Å
	wt. %			
$Zr_{0.7}Nb_{0.3}C_{0.54}$	6.6	-	-	4.697
$Zr_{0.6}Nb_{0.4}C_{0.39}$	4.85	-		4.666
$Zr_{0.5}Nb_{0.5}C_{0.42}$	5.15	-	-	4.645
$Zr_{0.8}Nb_{0.1}C_{0.62}H_{0.0.37}$	7.17	-	0.37	4.736
$Zr_{0.7}Nb_{0.3}C_{0.61}H_{0.24}$	7.04	-	0.24	4.696
$Zr_{0.7}Nb_{0.3}N_{0.33}H_{1.06}$	-	4.40	1.08	4.602
$Zr_{0.5}Nb_{0.5}N_{0.34}H_{1.00}$	-	4.60	0.99	4.561
$Zr_{0.7}Nb_{0.3}C_{0.44}N_{0.3}O_{0.1}$	5.44	4.07	0.10	4.680
$Zr_{0.5}Nb_{0.5}C_{0.38}N_{0.35}H_{0.2}$	4.18	4.52	0.20	4.583
$Zr_{0.4}Nb_{0.6}C_{0.36}N_{0.32}H_{0.2}$	4.55	4.98	0.25	4.624

In the Zr-Nb-C-N system, with rich Zr contents the combustion reaction with nonmetals is run by Zr, whereas Nb may be regarded as a diluent at the initial combustion stages. Rich Zr compositions form mainly a carbide phase after the combustion, with a decrease in the Zr content ZrN becomes the basic phase, and its subsequent reduction leads to an NbC phase being predominantly obtained.

We now consider the role of nonmetal components in the systems under study. In the complex carbide systems xZr + (1-x)Nb + yC, a reduction in the carbon fraction causes a decrease in the combustion temperatures and rates at any ratio of the metals and the formation of single-phase products. An increase in mixture "nonstoichiometry" leads to mutual dissolution of the two carbides. The combustion limits of this system as to carbon are less than 0.4 at. frac. for any Zr/Nb ratios.

In the Zr-Nb-C-H system, with decreasing carbon fraction in the mixture, the combustion reaction proceeds only in a low-temperature mode, starting with the composition 0.9Zr + 0.1Nb + 0.3C. With a reduction in the carbon fraction, starting with [C] = 0.6 at. frac., hcp carbohydrides form, and the hydrogen content increases in this case.

With a buildup of the gas pressure in the Zr-Nb-C-H system, the combustion temperatures rise, whereas the concentration of absorbed nitrogen in the final products decreases.

Introducing nitrogen into the Zr-Nb system allows SHS to be realized for all metal/carbon ratios, i.e., it extends the ignition region.

Of great interest are the regularities revealed in the interaction of metals with a mixture of nitrogen and hydrogen gases. Here, the reactions can proceed with the formation of nitrides, hydrides, or hydridonitrides, depending on P_{N_2}/P_{H_2}. With these possible reactions, it makes sense to dwell on the reaction of two-stage formation of hydridonitrides that occurs under conditions of competition of the reacting gases, much as that studied previously in the Zr-N-H and Ti-N-H systems.

In studying multicomponent systems, some interesting phenomena associated with the influence of hydrogen were disclosed. Conducting SHS in the Zr-Nb-C system in a hydrogen atmosphere allowed combustion to be realized throughout the range of metals-to-carbon ratios considered. The hydrogen pressure is one of the criteria determining the combustion mode in this case: when $P_{H_2} < P_{cr}$, the reaction proceeds in a high-temperature mode with the formation of complex carbohydrides, whereas when $P_{H_2} > P_{cr}$, it proceeds in a low-temperature mode with the formation of hydrides, similarly to the previously studied Me-C-H system.

With reignition of the preliminarily obtained combustion products of the Zr-Nb-N system in a hydrogen atmosphere (P_{H_2} = 10 atm), the content of bound nitrogen is reduced and T_c is no higher than 600°C. Here, single-phase hydridonitride of fcc structure are discovered in the products for the first time. In fact, during combustion in hydrogen, homogenization of multiphase combustion products occurs. The homogenizing action of hydrogen was also observed in the combustion of xZr + (1-x)Nb + yC in a nitrogen-hydrogen mixture under conditions of competition of gases.

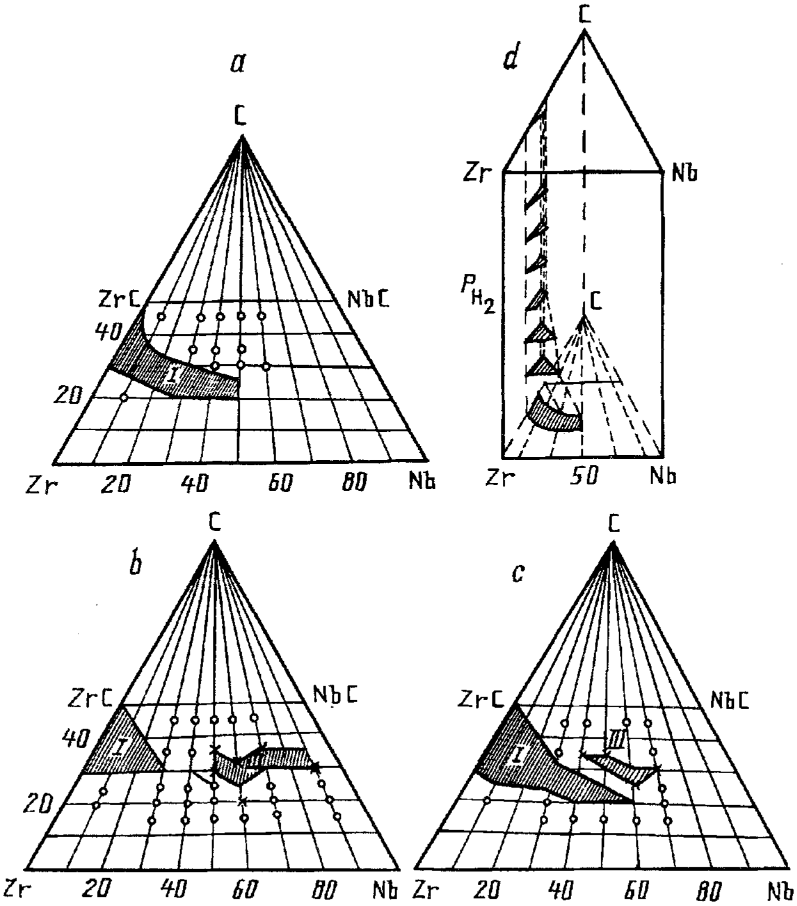

Fig. 1. Diagram of the phase composition for the systems: a) Zr-Nb-C, b) Zr-Nb-C-N, c) Zr-Nb-C-N-H, d) Zr-Nb-C-H.

The effects of individual reagents on combustion were described above. In reality, however, the characteristics of the combustion and the final products depend on the complex influence of all mixture components as a function of their quantity and reactivity.

In studying combustion processes in the Zr-Nb-C, Zr-Nb-C-H, Zr-Nb-C-N, and Zr-Nb-C-N-H systems, the principal conditions of the synthesis of single-phase and multiphase products are determined. All the data are plotted on the concentration triangle of the Zr-Nb-C system. Our triangular diagrams are not constructed under isothermal conditions. Each point of a diagram has its T_c inherent in a concrete concentration of the components. Taking into account that SHS reactions are transient (1-15 cm/sec) and cooling of the products from high temperatures occurs in a few minutes, it may be assumed that the products are quenched to some extent, each at its combustion temperature. Clearly, such a representation cannot be considered as an isothermal section of a triple diagram of state. Nevertheless, this data representation admits a comparison with known diagrams of states of the indicated system with certain reservation.

Figure 1 gives results obtained for the combustion of the Zr-Nb-C system in an argon atmosphere. We considered the part of the concentration triangle where combustion is realized, i.e., the region between 50 and 20 at. % carbon bounded by the beam section Zr:Nb = 40:60. The region of the single-phase complex carbide of variable composition $Zr_xNb_{1-x}C_y$ is hatched and marked by the numeral 1. Beyond it, the two-phase fields $Zr_xNb_{1-x}C_y$ + Zr and Zr_xNb_{1-x} + NbC_z are recorded. It should be noted that a continuous series of solid solutions is not observed within the limits of combustion of the system in question in the ZrC-NbC section. Three-phase SHS products are not found in this system either.

Of interest is the evolution of the phase composition of the products in the combustion of this same system with the participation of nitrogen (Fig. 1b) and in a nitrogen-hydrogen mixture (Fig. 1c). As is seen from Fig. 1b, the introduction of nitrogen allowed a broadening of the concentration limits of combustion of the system, i.e., combustion is realized over the entire range of metal ratios and of concentrations as to carbon. In region 1, which narrowed appreciably due to the introduction of nitrogen into the system, single-phase carbonitrides of variable composition $Zr_xNb_{1-x}C_yN_z$ form. In the two-phase region, apart from zirconium and niobium carbonitrides either the ZrN_x phase or the NbC_x phase is detected, depending on the Zr/Nb metal ratio. Here a third, three-phase, region also appears, mainly at the lower right-hand corner of the triangle, where the niobium fraction is large.

In the combustion of the Zr-Nb-C system in the nitrogen-hydrogen mixture it appeared that hydrogen, while competing with nitrogen, leads to a narrowing of the combustion region and facilitates an extension of single-phase region I, and here three-phase region III also narrows, i.e., under the action of hydrogen, "homogenization" of the products occurs: some three-phase products transform to two-phase ones, and a part of the two-phase products, to single-phase ones.

The phase composition diagrams for the Zr-Nb-C-H system are brought together as a prism (Fig. 1d), along whose height the hydrogen pressure increases from 1 to 100 atm. The concentration triangle Zr-Nb-C ($P_{H_2} = 0$) lies at the base of the prism. The region of single-phase carbohydrides, presented in a horizontal section, shifts and narrows with a buildup of the hydrogen pressure. In the concentration prism, a spatial region is isolated, each point on the surface of and inside which corresponds to a single-phase complex carbohydride with an fcc lattice. Beyond this region, the combustion products are multiphase, i.e., in the indicated spatial region, only single-phase carbohydrides that depend simultaneously on Me/Me'', C/Me, and P_{H_2} form.

Thus, the diagrams obtained demonstrate well the results for the combustion of multicomponent systems and allow the separation of various regions of SHS reactions that give rise to some final products.

NOTATION

x, y, atomic fractions of metals and carbon; P, partial pressure; T_c, combustion temperature; u_c, combustion rate; fcc, face-centered cubic; hcp, hexagonal close-packed.