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INFLUENCE OF ULTRASOUND VIBRATIONS ON THE PROCESS OF SYNTHESIS AND THE FINE STRUCTURE OF COMBUSTION PRODUCTS IN THE TITANIUM-SILICON SYSTEM

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The burning rates and maximum combustion temperatures as functions of the ultrasound vibration amplitude are given for mixtures of titanium-silicon powders with different ratios of the initial components. The results of measurements of the crystal lattice parameters of the synthesized phases (Ti_5Si_3 and $TiSi_2$) are given. It is inferred that the use of ultrasound vibrations in the process of self-propagating high-temperature synthesis provides a method for controlling the crystalline structure of the synthesized materials.

One of the most promising methods of producing inorganic refractory compounds is the method of self-propagating high-temperature synthesis (SHS) [1], based on using the energy of exothermic interaction of condensed materials with formation of solid-phase final products. The synthesis is in the form of combustion of heterogeneous systems, and the process of propagation of a synthesis wave itself has a complex nature due to multiple stages of the transformation process, which are connected with a change from the state of aggregation of the initial products to the final products in the combustion wave, inhibition of the chemical reactions, the formed synthesis products, and the processes of complete reaction and structure formation of the final products. It was as early as 1981 that A. G. Merzhanov pointed out that whereas by using SHS it is fairly easy to synthesize a new product it is by no means easy to bring it to the required "conditions," i.e., to manufacture a material with prescribed composition and properties. General ideas of the process prove to be insufficient. To do this requires a fundamental understanding of the combustion mechanism and numerous experiments. Producing combustion products of specified structure and material composition mainly depends on the initial compositions and the degree of dispersion of the components. Therefore, to control the process of structure formation of the final products, it is necessary to use methods of external action. One of the methods of this action on the SHS process is powerful ultrasound [2]. Due to nonlinear effects occurring in the material, the physicomechanical properties of the sounded material change under the action of ultrasound vibrations (USV), and the action of USV on the SHS process may lead to irreversible changes of both the thermal structure of the combustion wave and the processes of structure formation of the synthesis products.

The works on investigating the influence of USV on the combustion wave of the titanium-carbon system carried out earlier showed that applying USV leads to a change in both the combustion wave temperature profile (expansion of the zones of heating and chemical reactions and of the high-temperature portion of the zone of complete reaction) and the degree of carbon saturation of the carbide [3].

The titanium-silicon system is characterized by the presence of a large number of phases and, depending on the mixture composition, it is possible to produce both a single-phase final product and a multiphase one, and therefore investigation of the combustion process of this system under the ultrasound action is of both scientific (in terms of investigating the influence of ultrasound on the mechanism of combustion and structure formation of the produced product) and practical (as a method of active influence of it on the structure and phase composition of the produced materials) importance.

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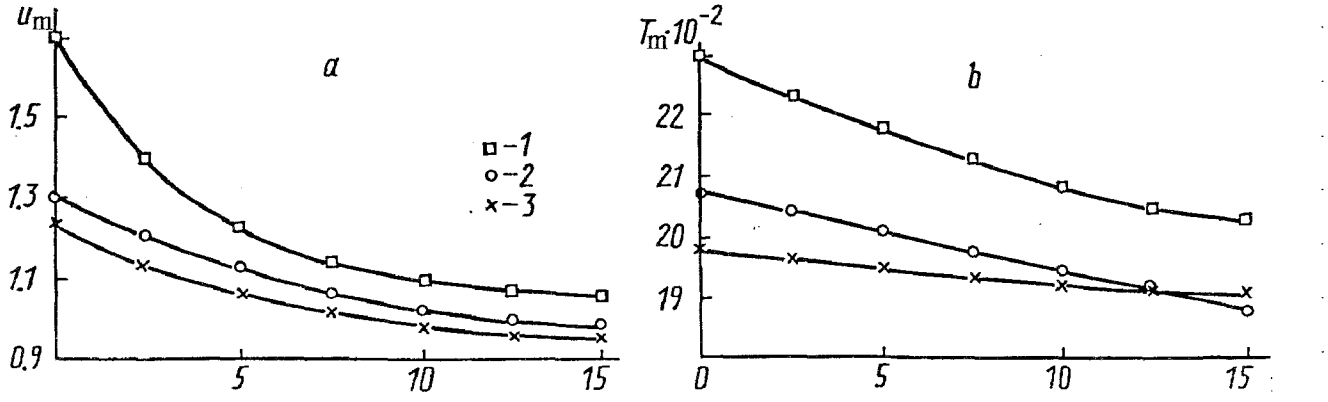

Fig. 1. Curves of a change in the combustion parameters of mixtures titanium–silicon with various component rations: 1) 0.6; 2) 0.5; 3) 0.8 and USV amplitude. u_m, cm/sec; T_m, k; ξ, μm.

The influence of USV on the level of burning rates and maximum combustion temperatures for Ti+βSi mixtures (β is the stoichiometric coefficient) was studied when varying the initial composition of the mixture [4].

The synthesis was carried out in an argon medium at a pressure of 1 MPa. The ultrasound vibrations were produced by a PMS-15A-18 magnetostriction converter fed from a UZGZ-4 ultrasound generator. The waveguide vibration amplitude was controlled during the synthesis by a feed-through electrodynamic sensor consisting of a two-section coil placed in a ring magnet of cobalt-samarium alloy. The amplitude sensor was calibrated using a micron indicator. During the experiments the specimen was mounted on the end of the waveguide. The acoustic contact was produced using weights. Between the specimen and the weights there was a spring serving as an acoustic duplexer. The burning rate was determined by a photographic method, using an FR-11 photorecorder, and from gas release by a DD-10 pressure pickup. The temperature along the combustion wave was measured by thermocouple and optical methods. In the first case the temperature of the burning specimen was measured by VR 5/20 tungsten-rhenium thermocouples 30 μm in diameter introduced into the specimen mass as deep as 5-10 μm (depending on the specimen diameter). The electric circuit was graduated using a PP-63 millivoltmeter. In the second case the temperature along the combustion wave was determined by the method of spectral relation for two wavelengths - 0.400 and 0.538 μm. All optical and electric BIT systems, including the photoelectric radiation detectors (FÉU-68), were graduated in brightness temperatures using an SI-6-100 standard tungsten lamp.

In the work use was made of powders of PTM titanium ($r < 100$ μm) and KPS-3 semiconductor silicon ($r < 63$ μm). The powders were previously dried in a vacuum cabinet at a temperature of 100°C for at least 10 h and were mixed in a ceramic mortar with subsequent mixing in a Turbula mixer for 4 h. Then, to improve the mechanical strength, a binder was introduced into the powder mixture. The binder content did not exceed 2% of the specimen weight. It is experimentally established that this amount of binder does not lead to a change in the burning rate or the combustion temperature. From the produced mixtures we manufactured specimens 10 and 20 mm in diameter and 15-20 mm high by a method of blind compaction; the relative density of the specimens was 0.6-0.65.

Figure 1 gives the obtained burning rates (a) and maximum combustion temperatures (b) for mixtures with different ratios of the components as functions of the USV amplitude. Analysis of the curves shows that, whatever the component ratio in the initial mixture, the action of ultrasound leads to a substantial change in the levels of the burning rates and the maximum combustion temperatures, and the character of change in the burning rate and the maximal combustion temperature is unique: with decreasing burning rate the maximum combustion temperature decreases simultaneously.

To explain the results obtained, the following mechanism of the combustion process under the action of USV can be proposed. In the heating zone in the compacted specimen there are always point contacts between the particles of the initial mixture. Therefore when applying USV under the action of alternating stresses local heating of the initial mixture occurs in the places of contacts, which may lead to formation of intermediate synthesis

TABLE 1. Crystal Lattice Parameters of the Ti_5Si_3 Phase as Functions of the Ultrasound Vibration Amplitude

Composition	A, μm	a, Å	c, Å	c/a	Composition	A, μm	a, Å	c, Å	c/a
Ti+0.5Si	0	7.425_8	5.148_0	0.693_3	Ti+0.6Si	0	7.420_0	5.154_0	0.694_6
	5	7.422_5	5.142_9	0.692_9		5	7.433_3	5.157_7	0.693_9
	10	$7,424_0$	5.142_9	0.692_7		10	7.428_6	5.158_6	0.694_4
	15	7.428_0	5.146_9	0.692_9		15	7.425_1	5.161_5	0.695_1
Ti+0.8Si	0	7.411_5	5.171_5	0.697_8	Ti+1.0Si	0	7.419_6	5.135_9	0.692_3
	5	7.424_6	5.144_2	0.692_9		5	7.419_5	5.136_5	0.692_3
	10	7.425_7	5.146_8	0.693_1		10	7.421_0	5.140_0	0.692_6
	15	7.428_0	5.144_0	0.692_6		15	7.423_3	5.142_4	0.692_7

$a_m = 7.4290$ Å; $c_m = 5.1392$ Å; $c_m/a_m = 0.6918$

TABLE 2. Crystal Lattice Parameters of the $TiSi_2$ Phase as Functions of the Ultrasound Vibration Amplitude

Composition	A, μm	a, Å	b, Å	c, Å	Composition	A, μm	a, Å	b, Å	c, Å
Ti+0.8Si	0	8.256_4	4.771_0	8.669_0	Ti+1.0Si	0	8.255_0	4.771_5	8.660_3
	5	8.256_7	4.77_57	8.670_8		5	8.255_6	4.771_8	8.665_2
	10	8.261_8	4.777_8	8.672_0		10	8.258_4	4.773_0	8.666_4
	15	8.263_3	4.777_0	8.670_6		15	8.261_9	4.774_6	8.668_9

$a_m = 8.2400$ Å; $b_m = 4.7800$ Å; $c_m = 8.5400$ Å

products in the heating zone. Furthermore, the action of USV leads to a change in the hydrodynamics of melt spreading. In this case in the chemical interaction zone due to a large amount of intermediate synthesis products entering it as a result of the change in the conditions of the chemical interaction a smaller amount of heat will be released than in combustion of mixtures without application of ultrasound, which manifests itself in the observed decrease of the maximum combustion temperature and the burning rate. This is indirectly confirmed by the results of X-ray investigations of the sounded specimens. Sounding leads to enlargement (inflation) of the crystal lattice of titanium.

The specimens produced were investigated by a method of X-ray structural analysis [5]. The X-ray investigations of the phase composition and crystal lattice parameters were carried out on an ADP-M6000 automated diffractometer with a Carl Zeiss Jena HZG-4 goniometer. CuK_α radiation was used, and the wavelength was taken to be the weighted average from the K_α doublet: $\lambda = 1.5418$ Å. The anode voltage was 35 kV, and the anode current was 15 mA. Graphite was used as a monochromator of radiation. The specimens for the X-ray investigations were ground into powder in a jasper mortar to the particle size $r \leq 100\ \mu$m.

For the phase analysis the following procedure was used:

1. Threefold scanning with a velocity of 3 deg/min in the range of angles 2θ (20-140°) with digital processing of information.

2. Search for X-ray reflections according to a program that analyzes all local intensity maximums and estimates the error probability when accepting a hypothesis that the given maximum is a peak. The criterion of hypothesis rejection ensured an error probability of at most 25%. This procedure was repeated for each scanning, after which reflections coinciding three times were selected with arithmetical averaging of the peak location.

3. Preliminary identification of the experimental spectrum by correlation with standard spectra from some base of standards. For this purpose use was made of a JCPDS card index containing approximately 4×10^4 standards. Interpretation was carried out according to a program realizing the Bayes algorithm, i.e., first from the JCPDS card index the cards of standards satisfying the preliminary criteria, for example, the presence of two of three strongest standard lines, were selected; then if the combination of standards overlapped all spectral lines, the minimum set overlapping the entire spectrum was selected from them.

4. Subsequent refinement of the assumed phases using photography by points after the accurate position of the line of the assumed phase is calculated with a scanning step of 0.02 deg; the exposure time at a point is 15-60 sec.

To determine the crystal lattice parameters, separate peaks belonging to the given phase were photographed stepwise. Prior to calculating the crystal lattice parameters preliminary processing of the line profiles was performed, which includes highlighting the background and smoothing the interpolating spline by an algorithm. Then the crystal lattice parameters were calculated from all possible sets of lines. From the obtained values of the crystal lattice parameters the maximum deviation from the standard was rejected, and the remaining values were averaged.

In X-ray phase analysis it was established that applying USV to the process of synthesis leads to a change in the diffraction reflection profiles and a shift of their centers of gravity. The resultant position of the centers of gravity of the diffraction lines, as a rule, approached, on the average, the standard values of the peak locations as the VS vibration intensity increased.

To estimate the influence of the value of the USV amplitude on the crystalline structure of the products, the crystal lattice parameters of the phases Ti_5Si_3 and $TiSi_2$ were determined by stepwise recording of the lines of these phases. Tables 1 and 2 give the results of calculations of the crystal lattice parameters of the Ti_5Si_3 and $TiSi_2$ phases, respectively.

Tables 1 and 2 show that the products produced under ordinary conditions (without the action of USV during synthesis) have a distorted crystal lattice as compared to the standard. Applying USV to the synthesis process leads to a change in the crystal lattice parameters of the synthesized phases, and the crystal lattice parameters of the Ti_5Si_3 phase approach the standard values and those of the $TiSi_2$ phase drift from them. The most nonmonotonic change in the crystal lattice parameters of the Ti_5Si_3 phase is obtained on the composition Ti+0.6Si. This probably can be explained by the fact that the combustion temperature of the composition is lower that the melting temperature of the Ti_5Si_3 phase, and therefore the forming skeleton of the Ti_5Si_3 phase experiences large alternating stresses. However, since the nonlinear effects appearing under ultrasound action have threshold values of the acoustic stresses, this must also have an effect on the fine structure of the crystal lattice.

Thus, it may be inferred that applying ultrasound vibrations to the SHS process leads to changes in the parameters that characterize the process of combustion (the burning rate and the maximum combustion temperature) and the crystal lattice parameters of titanium silicide, i.e., the action of ultrasound vibrations on the SHS process can be used as a method to control the process of synthesis.

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