

THERMAL SYNTHESIS UNDER THE CONDITIONS OF ELECTRIC PULSE HEATING

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The process of thermal synthesis caused by direct passage of a brief electric current pulse through a thermally reacting mixture of powders is considered. The Ti-Si, Ni-Si, Ti-C, and Ni-Al systems with different stoichiometries of the components in a powder mixture were investigated. The influence of the electric power parameters of the effect on the process of thermal synthesis is determined. The samples obtained were subjected to metallographic and X-ray-diffraction phase analysis, thus allowing one to identify chemical compounds characteristic for the indicated systems.

The present paper considers the process of thermal synthesis by direct passage of a brief electric current pulse through a thermally reacting mixture of powders. The excitation of an exothermal reaction is effected by the release of Joule heat in the contact zones of particles serving as centers for the origination of a thermal explosion.

Experiments were conducted on an electric-pulse setup whose schematic is presented in Fig. 1. In such a process the electricity stored in a bank of capacitors passes, in the course of bank discharge, through a thermally reacting mixture of powders poured into an insulating mold. To visualize the process of thermal synthesis, the mold was made of quartz glass or the mixture was subjected to preliminary pressing, and the samples were made in the form of porous cylinders. The setup was equipped with recording systems making it possible to measure the length and amplitude of the current pulse, as well as the discharge voltage.

The process of thermal synthesis was accompanied by a bright flash. The light flux from the side surface of the sample through a light guide and transformer arrived at a storage oscilloscope, which recorded changes in temperature both during mixture combustion and during the cooling of the product.

To obtain the compounds NiAl, Ti_5Si_3 , Ti_3Si , NiSi, Ni_3Si_2 , and Ni_2Si , powder mixtures corresponding to stoichiometric ratios were poured into glass molds to whose end faces electrodes were attached.

To obtain compact specimens made from titanium and nickel silicides, sialon molds were used.

X-ray analysis made it possible to determine that the main phases in the products were the corresponding stoichiometric compounds.

When the additive density of thermally reacting nonporous mixtures was calculated, we could see that it was lower than the density of the corresponding chemical compounds. Consequently, the excess of the sample over that of the additive mixture can serve as an indicator of the presence of a compound in the sample (see Table 1). After the experiments, the samples were compact tablets.

Of special interest is the dependence of the density of the samples on the discharge voltage at constant pressure (Fig. 2). As follows from the figure, up to a voltage of 2 kV only compaction of the mixture without a chemical reaction between the components takes place. At a higher voltage, the samples contain the compound Ti_3Si . This is confirmed by the results of metallographic and X-ray phase analysis, which revealed the presence of the Ti_3Si phase only in samples obtained at a voltage above 2 kV.

A sharper dependence is noted for Ni_2Si , where a density jump is observed in the narrow range 2.1-2.2 kV.

The process of combustion of the powder mixture Ti+C was investigated with the recording of temperature on preliminarily pressed cylindrical samples of diameter 11 mm and height 18 mm. The porosity of these samples amounted to 35%.

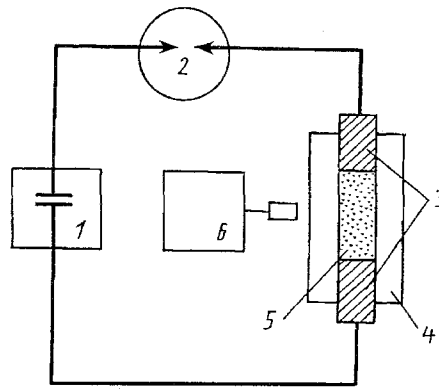


Fig. 1. Schematic of an electric-pulse setup: 1) bank of capacitors; 2) spark gap; 3) electrodes; 4) mold; 5) thermally reacting mixture; 6) system of temperature recording.

TABLE 1. Relationships among the Densities of Chemical Compounds, Stoichiometric Nonporous Mixtures, and Samples Obtained

Compound	Density, g/cm ³			
	γ_c	$\nu\Sigma$	γ_s	$\frac{\gamma_s}{\gamma_c} \cdot 100\%$
NiSi	5.93	4.64	5.28	89.0
Ni ₃ Si ₂	7.86	6.36	7.45	94.7
Ni ₂ Si	7.41	5.73	6.82	92.0
Ti ₅ Si ₂	4.31	3.63	4.10	95.1
Ti ₃ Si	4.60	3.91	4.42	96.1

According to [1], the adiabatic period of the thermal explosion induction is defined as the time needed for attaining the maximum reaction rate:

$$t_{ia} = \frac{CRT_0^2}{QEK_0} \exp(E/RT_0). \quad (1)$$

The higher the activation energy of the process, the smaller the difference between the maximum temperature and the temperature of the reaction rate maximum.

The temperature produced by electric-pulse heating of a sample can be obtained from the heat balance equation

$$C\gamma \frac{dT}{dt} = \rho j^2, \quad (2)$$

whence

$$T_0 = \frac{\rho_0 \int_0^{\tau_0} j^2(t) dt}{C\gamma}. \quad (3)$$

Taking logarithms in Eq. (1) gives

$$\ln\left(\frac{t_{ia}}{RT_0^2}\right) = \ln\left(\frac{C}{QEK_0}\right) + E/RT_0. \quad (4)$$

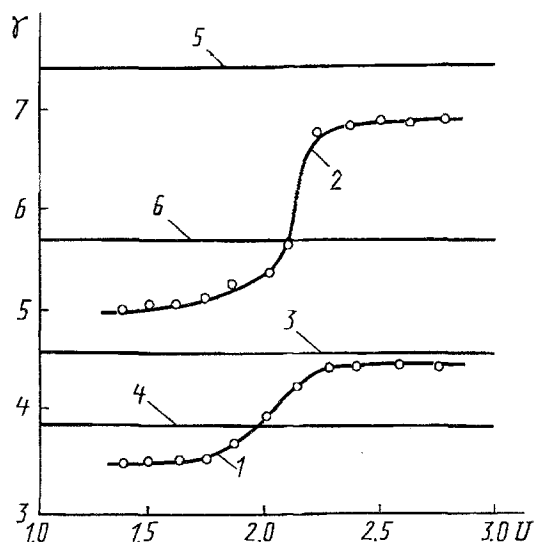


Fig. 2. Dependence of the density (g/cm^3) of samples of the mixtures 3Ti+Si at a pressure of 180 MPa (1) and 2Ni+Si at a pressure of 260 MPa (2) on voltage (kV); 3) density of the compound Ti_2Si ; 4) density of the nonporous mixture 3Ti+Si; 5) density of the compound Ni_2Si ; 6) density of the nonporous mixture 2Ni+Si.

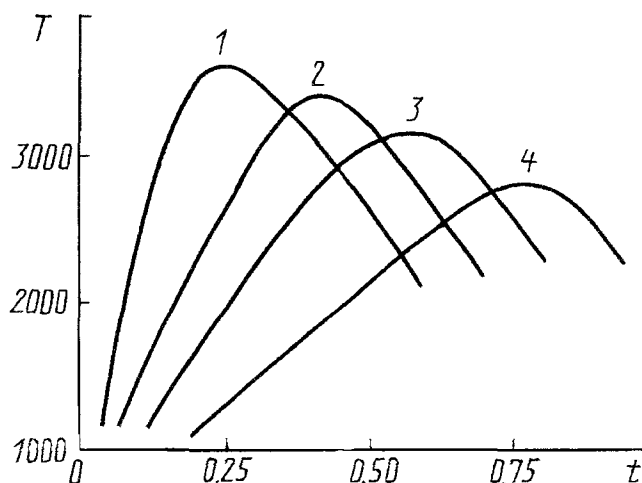


Fig. 3. Characteristic change in the sample temperature (K) as a function of time (sec) for different initial temperatures T_0 : 1) $T_0 = 880$ K; 2) 670; 3) 570; 4) 480.

whence the activation energy is determined graphically from the slope of the dependence of $\ln(t_{ia}/RT_0^2)$ on $1/T_0$ [2]. In this case T_0 is calculated from Eq. (3) with allowance for the initial room temperature of the sample.

In Fig. 3 the change in the sample temperature with time is presented.

Calculation by the least-squares method gives an activation energy of 50 kcal/mole, which is similar to the value obtained in [3] in the temperature range from 1500 K to the titanium melting temperature.

After thermal synthesis the samples were subjected to X-ray phase analysis, which revealed the presence of the basic phase TiC with the lattice parameter 4.327 Å, which satisfactorily agrees with literature data [4]. The presence of the TiO_2 phase was also detected, which can be explained by the fact that the experiment was run in air. The microstructure of the sample represented a porous medium consisting of TiC and small inclusions of free carbon. It seems that the residual carbon is present because a portion of the titanium is oxidized during the reaction and yields the compound TiO_2 .

NOTATION

γ_{Σ} , calculated additive density of mixtures; γ_c , density of the corresponding silicides; γ_s , maximum density of the samples obtained; t_{ia} , adiabatic period of the induction of a thermal explosion (induction time); C , heat capacity; Q , thermal effect of a reaction; E , activation energy of a process; R , gas constant; K_0 , pre-exponential factor; T_0 , initial temperature; ρ , specific electric resistance; γ , density of pressing; j , current density; τ_0 , duration of a current pulse.

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