

Specific Features of Solid-Phase Reactions Induced by Shock Waves

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Kinetic and thermodynamic aspects of solid-phase reactions in recovery ampoules under shock compression are considered. Attention is paid to incompleteness of chemical conversion owing to the “cold” character of exothermic reactions in shock waves and to the dependence of the heat-release profile on the grain-size distribution of reagents. Different degrees of conversion at an identical level of pressure under loading and unloading are noted.

Key words: shock waves, solid-phase reactions, recovery ampoule.

FORMULATION OF THE PROBLEM

Chemical transformations of solids in recovery ampoules under high dynamic pressures often proceed with less than 100% yield [1–5]. No attention has been paid to this trivial result, though it is not clear why an exothermic reaction, once it begins in a shock-compressed mixture where experiments yield a $(30 \pm 10)\%$ degree of chemical conversion, does not initiate the process in the remaining portion of the sample contacting the hot zone.

For instance, the heat releases in the synthesis reactions $\text{Sn} + \text{S}$, $\text{Cr} + \text{S}$, and $\text{Zn} + \text{S}$ are 108, 156, and 192 kJ/mole [6], which corresponds, for specific heats of 49.3–46.5 J/(mole · K), to the adiabatic temperatures of 2190, 3250, and 4130 K, respectively. These mixtures, however, which react at $T = 520\text{--}400$ K under standard pressure, remain inert when they contact seemingly incandescent “neighbors” in a recovery ampoule at the moment of shock compression and in the post-regime.

This fact can be explained within the framework of the model of forced diffusion with allowance for the experimentally established time of solid-phase reactions in shock waves equal to $\approx 10^{-7}$ sec [7, 8] and the decrease in the thermal effect of the reaction Q down to zero with increasing pressure [9], i.e., the compound decomposes into constituents (SnI_4 [10], CO_2 and CS_2 [11], and FeS [12]). Let us evaluate the effect of both factors.

EFFECT OF HIGH DYNAMIC PRESSURE ON REACTION KINETICS

The reaction time in solids is known to be limited by the velocity of diffusion and mixing of reagent particles. For a heterogeneous mixture loaded by a dynamic pressure p , this velocity can be very high because it equals the difference in particle velocities of the reagents ($\Delta u_{12} = u_1 - u_2$), which depends on pressure [7]. In the forced diffusion model, the time needed for a particle of one component to diffuse through a particle of another component is

$$\tau = 2d/\Delta u_{12}, \quad (1)$$

where d is the particle diameter.

If the value of Δu_{12} is insufficient for a particle of a certain size to pierce another particle and the first particle only penetrates into the second particle, the reaction is incomplete. This partial mixing can lead to an insignificant decrease in pressure of the onset of the reaction, but the entire effect lies within the same order of magnitude, because the penetration depth can vary from zero to the particle diameter. With a further increase in Δu_{12} , partial penetration becomes complete, i.e., with a certain shift, we obtain the same result as though we consider only the case of complete diffusion of one particle through another.

Shock compression of mixtures $\text{M} + 2\text{Si}$, where $\text{M} = \text{Al}, \text{Ti}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W},$ or Fe , with the use of high explosives with detonation velocities of 4.4 and 7.3 km/sec in cylindrical recovery ampoules was considered in [13]. Based on available shock adiabats of the

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TABLE 1
Velocities of Sulphur and Tin Particles
and Their Differences

p , GPa	u , mm/ μ sec		Δu , mm/ μ sec
	S	Sn	
5	0.70	0.24	0.46
10	1.15	0.43	0.72
15	1.52	0.60	0.92
20	1.83	0.74	1.09
25	2.11	0.88	1.23
30	2.36	1.00	1.36
35	2.60	1.11	1.49
40	2.82	1.22	1.60
50	3.22	1.42	1.80
60	3.58	1.60	1.98
70	3.92	1.77	2.15

reagents, the differences Δu_{12} were calculated as functions of pressure; for particles of diameter $d = 44 \mu\text{m}$ used, the pressure in reactions of interaction of the elements were determined. Evaluating the pressure developed in different parts of the cylindrical ampoule, we found [13] the size of zones where shock-induced solid-phase reactions are possible, which is in qualitative agreement with experimental data.

Using the experimentally determined time of synthesis $\leq 10^{-7}$ sec under shock compression of the system $\text{Sn} + \text{S} \rightarrow \text{SnS}$, we find Δu_{12} on the basis of shock adiabats of components and reaction products [14] and the pressure necessary for complete mixing and chemical interaction of solid reagents.

The particle velocities of Sn and S and their differences for pressures of 5–70 GPa are listed in Table 1. As the particle size after the conventional technological grinding of crystals varies within 0–100 μm and their distribution in most cases examined at our laboratory obeys the normal Gauss law, we can calculate how many particles of each size (with a step of 5 μm) are contained in the total mass of the mixture $\text{Sn} + \text{S}$.

INFLUENCE OF THE HIGH DYNAMIC PRESSURE ON THE THERMAL EFFECT OF THE REACTION

Obviously, if the reaction proceeds at a high pressure, the components of the mixture and the reaction product are compressed, which requires the mechanical

TABLE 2
Mechanical and Thermodynamic
Parameters of the System Sn—S

Composition	B_0 , GPa	B'_0	V_0 , cm^3/m	E_a , kJ/mole	B_0V_0/E_a
S	17.3	5.0	11.68	277	≈ 1
Sn	54.2	5.2	16.29	301	2.93
SnS	63.7	6.0	29.00	685	2.70

work W_c to be spent. This mechanical work is expressed by the relation

$$W_c = (9V_0B_0/\eta^2)\{\eta(1-x) - 1\} \exp[\eta(1-x)] + 1\} \quad (2)$$

obtained by integrating the Vinet–Ferrante equation of state [15]. In this expression, V_0 and V are the initial and final volumes of the body [cm^3], $x = (V/V_0)^{1/3}$, B_0 is the bulk modulus [GPa], B'_0 is its derivative with respect to pressure, and $\eta = 1.5(B'_0 - 1)$.

The reaction $\text{Sn} + \text{S} \rightarrow \text{SnS}$ at a high pressure is accompanied by heat release whose magnitudes differs from the standard value of the thermal effect because of different compressibilities of the mixture and the compound. The work of compression is spent on heating, changing the real structure of the body, and increasing the chemical bond energy. If the compressibility of the mixture is higher than the compressibility of the compound, the increase in the energies of the bonds Sn–Sn and S–S is greater than the increase in the energy of the bond Sn–S; hence, the thermal effect of the reaction under a high pressure is lower than its standard value.

The energy of compression can be determined by comparing the work of compression extrapolated to zero pressure (B_0V_0) and the energy of atomization (E_a) of the components and reaction product under standard conditions. Obviously, this ratio can be only ≥ 1 . In our case, $B_0V_0/E_a = 1, 2.93,$ and 2.70 for S, Sn, and SnS, respectively. Experimental data necessary to calculate the work of compression are given in Table 2; the mechanical characteristics of sulphur are taken for the high-pressure phase, which is stable at $p > 5$ GPa.

Thus, to determine the change in the thermal effect of the reaction with increasing pressure (ΔQ), we have to calculate the value of W_c for sulphur, tin, and SnS and then find the algebraic sum

$$\Delta Q = W_c(\text{S}) + W_c(\text{Sn})/2.93 - W_c(\text{SnS})/2.70. \quad (3)$$

Table 3 contains the particle size d , the particle concentration C , the difference in particle velocities Δu_{12} sufficient for mixing of particles, the pressures corresponding to these differences, and the changes in the

TABLE 3
Thermal Effect of the Reaction Sn + S As a Function of Pressure

d , μm	C , %	Δu_{12} , $\text{mm}/\mu\text{sec}$	p_{12} , GPa	$-\Delta Q$	Q_p	ΔT , K	δT , K
				kJ/mole			
0-5	0.02	0.1	0.8	0.5	0.02	0.4	0.4
0-10	0.07	0.2	1.7	1.1	0.07	1.4	1.0
0-15	0.26	0.3	2.8	1.8	0.28	5.7	4.3
0-20	0.82	0.4	4.2	2.9	0.86	17.4	11.8
0-25	2.28	0.5	5.8	4.3	2.36	47.9	30.4
0-30	5.48	0.6	7.6	6.0	5.59	113	65.5
0-35	11.51	0.7	9.7	8.6	11.44	232	119
0-40	21.19	0.8	12.0	11.2	20.51	416	184
0-45	34.46	0.9	14.5	14.2	32.32	656	240
0-50	50.00	1.0	17.2	17.3	45.35	920	264
0-55	65.54	1.1	20.4	20.8	57.15	1159	239
0-60	78.81	1.2	23.8	24.7	65.65	1332	172
0-65	88.49	1.3	27.6	29.3	69.64	1412	80.9
0-70	94.52	1.4	31.6	33.6	70.32	1426	13.8
0-75	97.72	1.5	35.6	37.6	68.79	1395	-31.0
0-80	99.18	1.6	40.0	42.7	64.76	1314	-73.8
0-85	99.74	1.7	44.4	47.3	60.54	1228	-85.6
0-90	99.93	1.8	50.0	53.2	54.76	1111	-117
0-95	99.98	1.9	55.5	58.7	49.30	1000	-111
0-100	100	2.0	61.2	64.5	43.50	882	-118

thermal effect ΔQ for each value of pressure corresponding to initiation of chemical interaction of particles of a certain size.

The difference $Q - \Delta Q$ multiplied by the concentration of particles of a particular size yields the fraction of the thermal energy released as particles of increasing size become involved into chemical interaction (Q_p) (see Table 3), whereas the quotient of Q_p divided by specific heat yields the corresponding value of temperature. Depending on whether the temperature has enough time to become identical over the entire sample during the chemical synthesis period or not, however, the increase in temperature due to chemical heat release should be calculated either on the basis of the total value of Q_p at each stage (i.e., consecutive additions of temperature to a preheated body; ΔT in Table 3) or on the basis of the difference in Q_p for each pair of particles of the neighboring fractions (independent heating of each portion of the substance; δT in Table 3).

As is seen from Fig. 1, the thermal effect of the reaction decreases after a certain pressure; the dependence $\Delta T(p)$ is characterized by a maximum in accordance with the experiment of [8], though the absolute values of ΔT in the case of thermal equilibrium are much higher than those in the adiabatic variant.

EFFECT OF THE "HISTORY" OF HIGH DYNAMIC PRESSURE ON THE COURSE OF THE REACTION

There is one more issue. The thermal effect decreases with increasing pressure, i.e., the thermodynamic stimulus of the reaction decreases, whereas the dynamic pressure in the course of unloading decreases, and the reverse process should proceed: an increase in Q and in the degree of chemical conversion. In reality, however, something different occurs. If a 100% conversion occurs in a number of systems $M + 2\text{Si}$ at the axial

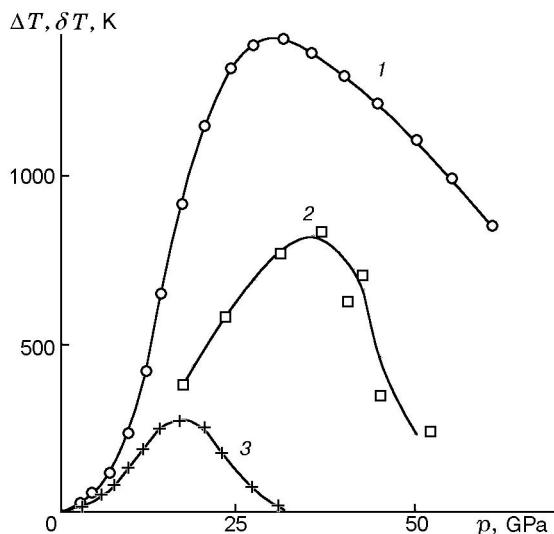


Fig. 1. Experimental and calculated heat-release curves versus pressure in the case of chemical interaction of tin and sulphur in the shock wave: curve 1 refers to ΔT from Table 3, curve 2 refers to experimental data of [8], and curve 3 refers to δT from Table 3.

part of a cylindrical ampoule, only partial formation of MSi_2 is observed as the shock-wave intensity decreases toward the periphery of the cylinder, and this process does not occur at all at the ampoule walls [13]. The same phenomena are observed in sulphide systems.

The model proposed can explain this fact. As the characteristic time of unloading of a shock-compressed body in laboratory experiments with explosive diameters of 40–60 mm is $\approx 10^{-6}$ sec, a decrease in dynamic pressure, e.g., from 100 to 1 GPa means a decrease in time of operation of high pressure within each gigapascals to $\approx 10^{-8}$ sec, which is insufficient for mutual diffusion of coarse reacting particles. The reaction of, e.g., interaction $\text{Cr} + \text{Te}$ can be supported by a severalfold increase in the explosive mass, other test conditions being identical [3].

Thus, solid-phase chemical reactions induced by shock waves proceed with different yields under an identical pressure, depending on the “history” of the latter, i.e., whether the optimal pressure is achieved directly by detonation of an appropriate high explosive and acts during 10^{-6} sec or it is achieved in the course of unloading from a higher level and, therefore, acts during a much shorter time at each stage.

CONCLUSIONS

Some issues are still not resolved. If the high pressure leads to a decrease in the thermal effect and the latter can completely disappear with a further increase

in pressure, what happens to the thermal effect of the synthesized substance after a decrease in pressure? If the loading–unloading process is reversible and a sufficient amount of heat is again released after a decrease in pressure, why does not it initiate a chemical reaction in the remaining portion of the unloaded mixture?

The answers to these questions require special investigations. In the first approximation, however, we can assume that the system during its unloading in the region of negative pressures can reach a certain additional minimum on the potential surface. None of the substances synthesized at our laboratory by explosive methods had a density equal to its standard value (see [3, 16, 17]). When an unloaded body is heated, its structure is improved with an exothermic effect, though even annealing cannot completely prevent shock-synthesized unification into a state commonly occurring under standard conditions. Hence, shock-induced synthesis leads to obtaining substances with a new set of properties, and the mere fact of partial proceeding of exothermic reactions under shock compression in recovery ampoules is another criterion for chemical interaction of solids in the zone of high dynamic pressures.

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