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SOLID-PHASE REACTIONS IN SHOCK WAVES: KINETIC STUDIES AND MECHANISM

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The change of molar volumes of condensed matter in synthesis reactions in solid state is considered and the volume of the system is shown to increase in exothermic processes. A more significant increase in volume is observed at high pressures. This is reflected on the shock pressure-volume curve of the reacting mixture. Measurements of the kinematic parameters of the reacting systems show that the chemical reaction proceeds to a noticeable extent in a time of less than 10^{-6} sec. *Temperature measurements made it possible to establish that the reaction time was less than* 10^{-7} sec. *A model is suggested for explaining the ultrarapid diffusion process and chemical interaction of solids. The model is based on hydrodynamic transfer (with velocities equal to the difference in the mass velocities of the reactants) of particles shattered by a shock wave. A degree of chemical conversion in the shock waves corresponds to the course of the chemical reaction over the surfaces of domains with a size of* $\sim$ 100 Å.

The chemical transformations resulting from shock compression were found as early as in the first experiments in which the substance exposed to the action of explosion was recovered [1]. Subsequent studies of chemical processes in shock recovery capsules (see [2]) not only led to important practical results but also posed a number of problems of a fundamental character. The most important of them is determination of the rate of a solid-phase chemical reaction under shock wave loading.

Skipping the numerous studies of shock interaction of condensed substances, a comprehensive account of which can be found in [3–12], we shall analyze the latest works devoted to measuring the kinematic and thermic characteristics of condensed reacting systems under dynamic loading in real time. It is these measurements that make it possible to develop models explaining the kinetics of solid-phase chemical reactions in shock waves and permitting one to plan the direction and prospects of further studies.

CHANGE OF MOLAR VOLUMES OF SUBSTANCES UNDER CHEMICAL TRANSFORMATION

The study of chemical transformations by measuring the compressibility of the reacting mixture is possible only when the process is accompanied by noticeable change in the volume of the system.

Speaking generally, phase transformations under high pressure must be accompanied by a decrease in the volume of a solid. If such a transformation leads only to a change in structure (phase transition of the first kind), there must be a segment of the pressure-volume curve (of different slope and size, depending on the depth and rate of transformation and on properties of the substance) that characterizes the degree of decrease in volume.

Since the enthalpy of a phase transition usually amounts to 10^{-4}–10^{-3} of the solid atomization energy E_a [13], the thermal component of the process introduces no noticeable corrections into the volume changes.

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TABLE 1

Volume Change Resulting from Formation of Compounds at Normal Pressure

Compound	V_0, $\frac{\mathrm{cm}^3}{\mathrm{mole}}$	$-\Delta V_r$, $\frac{\mathrm{cm}^3}{\mathrm{mole}}$	Q, $\frac{\mathrm{kJ}}{\mathrm{mole}}$	ΔV_Q, $\frac{\mathrm{cm}^3}{\mathrm{mole}}$	ΔV_0, $\frac{\mathrm{cm}^3}{\mathrm{mole}}$
NaCl	27.01	14.00	409.1	26.07	12.1
NaBr	32.15	11.22	361.7	28.71	17.5
NaI	40.83	8.49	293.0	31.26	22.8
CsCl	42.05	45.05	445.2	49.60	4.55
CsBr	47.72	41.74	407.3	49.36	7.62
CuCl	23.78	0.71	156.6	3.18	2.47
CuBr	27.74	−0.90	103.0	2.53	3.43
CuI	33.22	−0.43	65.9	1.70	2.13
CaO	16.76	19.97	646.5	9.21	−10.76
CaS	27.64	14.00	476.0	14.17	0.17
ZnO	14.19	5.42	339.3	2.00	−3.42
ZnS	23.78	0.74	203.3	2.05	1.31
ZnTe	34.00	−4.41	91.5	1.80	6.21
SnS	29.00	2.65	105.8	2.65	0
SnSe	32.55	0.16	88.7	3.60	3.44
SnTe	37.98	−1.28	62.0	3.37	4.65
AlN	12.55	5.21	311.0	2.98	−2.23

But if the loading results in a change in the chemical composition and the heat of reaction can reach 60–70% of E_a [14], then the heat release will lead to considerable expansion of the reaction product and, instead of decreasing, the volume of the system can increase.

As an example, consider the synthesis reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}, \tag{1}$$

where A is a metal of the 1st–3rd groups of the Periodic Table, and B is an element of the 5–7th B subgroups. Comparing molar volumes of the components of the mixture with that of the compounds on the basis of data from [15, 16], one finds that changes in volume resulted from reactions of type (1)

$$\Delta V_r = V_{\mathrm{AB}} - (V_{\mathrm{A}} + V_{\mathrm{B}}). \tag{2}$$

In Table 1, these changes are compared with their specific heats of reaction

$$Q = E_{\mathrm{AB}} - \frac{1}{2}(E_{\mathrm{AA}} + E_{\mathrm{BB}}), \tag{3}$$

where $E_{\mathrm{AA,BB,AB}}$ are the bond energies of atoms under normal thermodynamic conditions [14, 17]. The same table presents the values of volume growth caused by the heat released as a result of an exothermic reaction. The values were calculated from the equation

$$\Delta V_Q = Q_{\beta} V_{\mathrm{AB}}/c_p, \tag{4}$$

where c_p is the specific heat and β is the coefficient of cubic expansion, as given in [18–22].

The sum of the values of ΔV_Q and ΔV_r characterizes the total change in system volume that results from chemical interaction

$$\Delta V_0 = \Delta V_Q + \Delta V_r. \tag{5}$$

As seen from Table 1, in most cases, the formation of chemical compounds is accompanied by a decrease in volume, but heat release results in expansion of the system. Therefore, $\Delta V_0 > 0$, as a rule. However, it is good to bear in mind that ΔV_0 will correspond to the facts only if the reaction occurs instantly, so that the system has no time to cool. But if the reaction (a solid-phase one, for example) proceeds very slowly, the heat

TABLE 2

Volume Changes Resulting from Formation of Compounds at $p = 10$ GPa

Compound	$-\Delta V_r, \frac{\text{cm}^3}{\text{mole}}$	$Q, \frac{\text{kJ}}{\text{mole}}$	$\Delta V_Q, \frac{\text{cm}^3}{\text{mole}}$	$\Delta V_E, \frac{\text{cm}^3}{\text{mole}}$	$\Delta V_p, \frac{\text{cm}^3}{\text{mole}}$	$\frac{\Delta V_p}{V_p}$, %
NaCl	4.32	380.6	19.39	1.38	16.4	63.0
NaBr	2.74	338.7	20.97	2.19	20.4	73.1
NaI	1.84	273.8	21.71	4.16	24.0	74.4
CsCl	6.18	351.3	29.56	4.33	27.7	73.1
CsBr	4.56	319.0	28.58	5.58	29.6	74.3
CuCl	−0.64	149.7	2.53	0.34	3.51	18.3
CuBr	−2.47	95.4	1.98	0.44	4.89	23.2
CuI	−2.61	54.0	1.17	0.57	4.35	17.1
CaO	7.67	615.1	8.77	0.09	1.09	4.7
CaS	4.80	443.9	11.72	0.41	7.33	24.9
ZnO	−0.68	331.9	1.96	0.02	2.66	21.0
ZnS	−2.79	193.7	1.76	0.11	4.66	24.8
ZnTe	−5.53	89.4	1.52	0.38	7.43	36.4
SnS	−0.93	95.0	2.11	0.35	3.39	13.6
SnSe	−2.86	77.0	2.74	0.72	6.32	24.6
SnTe	−1.80	50.2	2.30	1.37	5.47	18.1
AlN	0.45	297.6	1.64	0.02	1.21	9.8

will be conducted into the surrounding medium and $\Delta V_Q \to 0$.

Let us analyze the synthesis reaction under high pressure. Given the compressibility of the components and reaction products (1), one can calculate the molar volumes, compression energies, and heats of reaction at any pressure. We will make calculations for $p = 10$ GPa.

Using the known values of the bulk moduli B_0 and their derivatives B_0' with respect to pressure [2], one calculates the compressibility of solids on the basis of the Vinet–Ferrante equation [23]

$$p(x) = p_t\,[(1-x)/x^2]\exp[\eta(1-x)], \tag{6}$$

where $p_t = 3B_0$ (p_t is the thermal component of the pressure); $\eta = 1.5\,(B_0' - 1)$; $x = (V/V_0)^{1/3}$; V_0 and V are initial and final volumes of the solid, respectively. Setting $p = 10$ GPa, we calculate the volume of the mixture and compound and then, from Eq. (2), ΔV_r. Since the compressibility of the elements is greater than that of their compounds (see [24]), we conclude that, as seen from Table 2, the following inequality holds for absolute values: $\Delta V_r\,(p = 10) < \Delta V_r\,(p = 0)$.

Integrating Eq. (6) yields the following expression for the compression energy

$$E_p = (3V_0 p_t/\eta^2)\{[\eta(1-x) - 1]\exp[\eta(1-x) + 1]\}. \tag{7}$$

If we calculate this energy for the initial components and reaction products, then the difference

$$E_p = [E_p(\mathrm{A}) + E_p(\mathrm{B})] - E_p(\mathrm{AB}) \tag{8}$$

(if it is positive) is the amount by which the heat of reaction decreases at high pressures. The specific heats of the reaction and values of ΔV_Q for $p = 10$ GPa, calculated from Eq. (4), are also given in Table 2.

Finally, Table 2 presents corrections (ΔV_E) for the increase in the volume of the compound AB resulting from its heating under shock compression at a pressure of 10 GPa. They, too, are calculated from Eq. (4), where the value of the increment of internal energy under shock compression is used instead of Q

$$dE = (1/2)\,[p\,(V_0 - V)]. \tag{9}$$

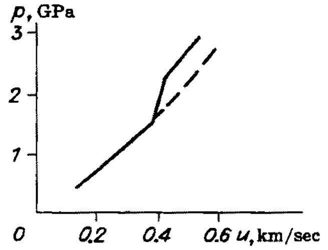

Fig. 1

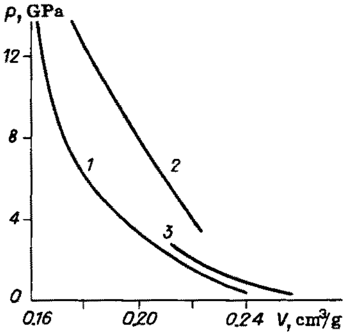

Fig. 2

Fig. 1. p–u dependence for TNT detonaton.

Fig. 2. Shock adiabat of $Pb(NO_3)_2$ + 5 % Al mixture. (1) refers to $Pb(NO_3)_2$, (2) to the reacting mixture, (3) to the inert mixture $Pb(NO_3)_2$ + Al.

The results of summation of all volume changes

$$\Delta V_p = \Delta V_r + \Delta V_Q + \Delta V_E \tag{10}$$

are given in the last column of Table 2 (here, V_p is the volume of the mixture at $p = 10$ Gpa). These values correspond to an adiabatic process. That is to say, theoretically, they are most adequate for reactions in shock waves.

Thus, shock compression of a mixture in which reaction is accompanied by heat release results in the formation of compounds with an average volume increase equal to 71% for alkali halides and 20% for the other compounds presented in Table 2. This means that the shock pressure-volume curve of a reacting mixture at the beginning of chemical transformation must show a deflection in the direction of increasing in volume.

KINEMATIC MEASUREMENTS

As a rule, the accuracy of measurements of the kinematic parameters D and u amounts to 1–2%. Therefore, the error in determining V is not less than 3–6%. For this reason, in most cases the deflections of the compressibility curves caused by chemical transformation can be found, as seen from the data in Table 2, only if the degree of reaction during the shock wave loading is greater than 30%.

In most favorable cases such as detonation processes, for example, the heat release and expansion of the system are so great that they can be easily registered in an experiment. As an illustration, Fig. 1 presents the dependence $p(u)$ for TNT detonation [25] and Fig. 2 shows the shock adiabat for a $Pb(NO_3)_2$ + Al mixture [26], which describes a process similar to detonation.

Registration of volume changes on the shock pressure-volume curves means that the reaction occurs in time $\tau < 10^{-6}$ sec. In the case of detonation, this fact is quite understandable, since the process is intramolecular and encounters no kinematic obstacles. If the chemical reaction proceeds at high pressure in the solid phase, diffusive limitations make such fast a process very problematic.

A study of the shock compressibility of Sn + S mixtures was started in our laboratory in 1969 [27] and completed in 1986 [28]. It was established that at $p \geqslant 15$ GPa the compressibility curve deflects toward a greater volume (Fig. 3a), though the magnitude of the effect is close to the experimental error (it is seen from Table 2 that $\Delta V_p = 13.6\%$ at $p = 10$ GPa and the measurement error approaches half of the effect at a reaction degree of about $\sim 30\%$). A more pronounced change in the Hugoniót curve Fig. 3b) was found while studying the Sn + Te reaction [29].

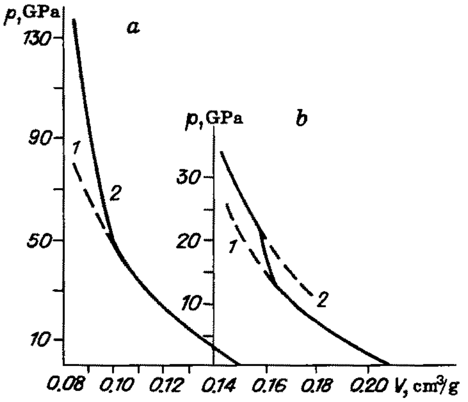

Fig. 3

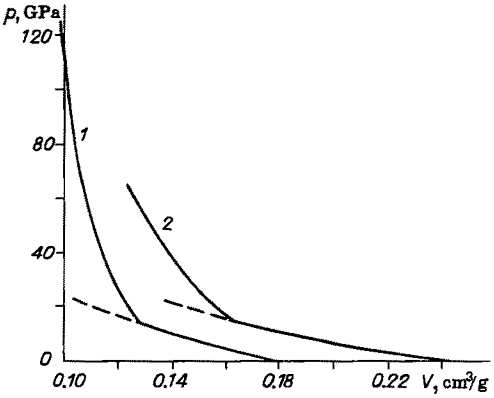

Fig. 4

Fig. 3. Shock adiabats of the system Sn/Te (a) and Sn/S (b): (1) refers to the mixture and (2) to the compound.

Fig. 4. Shock pressure-volume curves for CuI (1) and CuCl (2).

Establishment of the fact that the reaction of the interaction of condensed materials proceeds immediately behind the shock front should be regarded as a fundamental result of those experiments.

Both the magnitude of the effect and the threshold value of the reaction pressure depend on the experimental conditions: powder porosity, particle size, and loading-pulse duration. Because of this, one may fail to register any deflection on the pressure-volume curve in the process of shock compression under certain experimental conditions when the volume changes in the course of reaction are insignificant and the reaction is not completed (see [30]).

Phase transformations under shock compression of CuI [31] and CuCl [32] (Fig. 4) were found recently. We interpret them as reactions of disproportionation

$$2\,\mathrm{CuX} \rightarrow \mathrm{Cu} + \mathrm{CuX_2} \tag{11}$$

on the basis of volume relations in this system.

Indeed, the molar volumes of $CuCl_2$ and $CuBr_2$ are equal to 39.09 and 45.66 cm^3, respectively [33]. Taking into account the data of [15, 16] on the mole volumes of CuX and Cu, we obtain for the system

$$2\,\mathrm{CuCl} \rightarrow \mathrm{Cu} + \mathrm{CuCl_2}, \qquad \Delta V_r = 47.56 - (7.11 + 39.09) = 1.36\ \mathrm{cm^3/mole} \tag{12}$$

and for the system

$$2\,\mathrm{CuBr} \rightarrow \mathrm{Cu} + \mathrm{CuBr_2}, \qquad \Delta V_r = 55.48 - (7.11 + 45.66) = 2.71\ \mathrm{cm^3/mole}. \tag{13}$$

It should be noted that in the case of CuBr, decomposition in accordance with scheme (13) is established experimentally at high pressures [34].

Since the volume in chemical reactions increases because of heat release, it seems more promising to use the methods of direct thermal measurements by registering the start of chemical transformation at high dynamic pressures.

TEMPERATURE MEASUREMENTS

The first results of temperature measurements in the Sn + S system were published in [27]. The measurements were conducted with the aid of thermocouples 0.05–0.1 sec after the explosion of a loose-packed

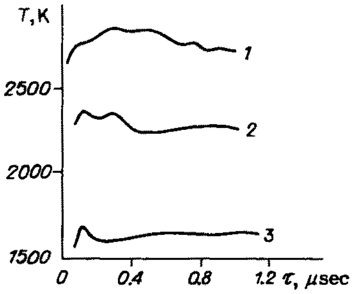

Fig. 5

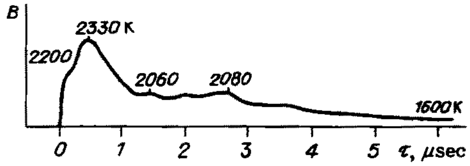

Fig. 6

Fig. 5. Change in time of brightness temperature in Sn+S mixture at $p = 44.7$ (1), 33.0 (2), and 25.3 (3) GPa.

Fig. 6. Change in intensity and brightness temperature in Sn + S mixture at $p = 40$ GPa.

RDX charge in cylindrical shock recovery capsules. Under identical experimental conditions, the values of the residual temperature T_{res} proved to be equal to 383, 393, and 403 K for Sn, S, and SnS, respectively, while for the Sn+S mixture T_{res} was found to be equal to 1380 K in the same conditions.

The lag of thermocouple measurements was subsequently decreased to 10^{-3} sec [35], then to 10^{-4} sec [36], and finally to a time of less than 10^{-4} sec [37] through the use of thinner wires and foils. However, a further decrease proved impossible, because of failure of the thermocouples. For this reason, an optical pyrometer was used to study shock chemical interaction in real time. Since the radiation intensity is $\sim T^4$, optical measurements of temperature seem to be most convenient for study of the kinetics and the mechanism of the chemical reactions in shock waves.

The brightness temperatures under shock compression of the Sn + S mixture, SnS, and pure sulphur were measured [30, 38] with the aid of a two-channel optical pyrometer at effective wavelengths of 720 and 420 nm with resolutions of 20 and 50 nsec, respectively. The intensities obtained were converted to brightness temperatures and averaged over the wavelengths. The measurement error did not exceed 150 K and the temperature difference at different wavelengths was even smaller.

In an inert medium, there occurs an increase in T up to the maximum value in a time close to the resolution time of the device, then the temperature drops by $\sim$ 200 K in $\sim$ 0.2 μsec, and afterwards it diminishes more smoothly.

The temperature change in the Sn + S mixture is of a different character (Fig. 5). Here, one observes either a constant radiation level after the first peak, or a monotonic increase in temperature for during $\sim$ 0.2 μsec followed by a constant level.

Figure 6 shows the change in the radiation intensity B in time and in the brightness temperature of the Sn + S mixture in characteristic record points. The temperature was determined in an experiment with a plexiglass window. Due to the large thickness of the soft window, information about the cooling of the reacting system was obtained in a time of less than 6 μsec. It is important that the temperature $T = 1600$ K measured by the optical method be close to the value found by the thermocouple method (= 1400 K) in a time of 10^{-2}–10^{-3} sec in the shock recovery capsules (see above). This indicates that the assumption of temperature homogeneity of the surface of the reacting mixture, used as the basis for mathematical treatment of the experimental results, is valid.

It is also important that the radiation level of the reacting system be considerably greater than the corresponding level for the inert sample under the same loading conditions (Fig. 7). A quantitative estimate of the reaction degree was made within the framework of the Mie–Grueneisen equations under the assumption that the Grueneisen coefficient, specific heat, and heat of reaction were constant. Under these assumptions,

TABLE 3

Shock Pressure and Temperature in Sn+S *Mixture*

p, GPa	T_{inert}, K	T_{exp}, K	ΔT, K
24.1	1035	1600	565
31.1	1465	2250	785
37.5	1975	2800	825
41.0	2230	2850	620
43.0	2400	3100	700
45.5	2580	2950	370
52.5	3260	3500	240

TABLE 4

Change in Cpecific Heat of Reaction (Q_0 = 106 kJ/mole) *with Pressure*

p, GPa	E_p, kJ/mole			Q_p, $\frac{\text{kJ}}{\text{mole}}$
	Sn	S	SnS	
15	12	26	26	94
30	46	56	71	75
50	91	94	143	64

processing of the experimental data yields a value of reaction degree of ~ 30%. As the pressure increases, the temperature of the system first grows and then drops (Table 3).

The bell-shaped curve of the increase in temperature due to heat release during the reaction (Fig. 8) indicates that two opposing trends are at work as p increases. On the one hand, the growth of pressure facilitates the formation of SnS, which proceeds with a decrease in volume (see also Table 1), but, at the same time, the heat of reaction decreases.

The role of the latter factor is reflected in Table 4, which presents values of compression energy calculated from Eq. (7) for the reacting Sn + S mixture and the reaction product SnS. It also shows the magnitudes of the heat of reaction decreased by ΔE_p [see (8)]. With respect to this decrease in the heat of reaction, one should expect the temperature of the reacting mixture to decrease as the pressure grows. As follows from Table 2, this pattern should be of a universal character.

Temperature dependences of the shock-interaction reactions of magnesium, aluminum, and titanium with sulfur in real time were studied in [39, 40]. The experimental values of temperature proved significantly higher than those calculated for inert compounds and pure sulfur. Pure sulfur has the highest shock compression temperature of all the original components. A chemical reaction in the mixtures of Mg, Al, and Ti with sulfur proceeds in 50 nsec behind the shock front, with the degree of reaction for Mg + S equal to ~ 0.2 and for Al + S to ~ 0.5. As the shock wave intensity in the latter system increases, the brightness temperature grows: $T = 2700$ and 3200 K at $p = 26$ and 40 GPa, respectively (Fig. 9).

Optical studies of the system Al + S allowed us to find the dependence of the glow intensity and kinetics of shock interaction on the dispersity of particles. It is seen from Fig. 10 that a more disperse substance reacts with a greater heat release; the temperature of the system grows during ~ 0.3 μsec and then gradually decreases during 0.8 μsec. The larger particles behave differently: at first (in 0.1 μsec), there is an abrupt burst of glow intensity, which is then followed by a rapid fall and slow growth.

These peculiarities indicate that the reaction proceeds on the surface of the particles; therefore, the chemical reaction is of a solid-phase character. In the case of large particles, the reaction ceases as soon as the available surfaces are used up. Further development of the process occurs with thermal diffusion of the atoms inside the particles or with release of their surfaces from a layer of already reacted substance, provided that the mechanical properties of the latter differ appreciably from those of the initial component.

Slow kinetics displayed itself clearly when the system of Mg + S with a plexiglass window was studied. If it is loaded with a cast TNT–RDX explosive, after the primary peak one observes a secondary gradual growth of temperature, which occurs as a result of development of the process after the pressure fall (Fig. 11). This case models a situation in the recovery capsule.

In all of the above-listed cases, the shock-compression temperatures exceed considerably those of the inert mixtures. This must reflect on the pressure profile. Figure 12 presents the profiles in an Al + S mixture and in the constituents Al and S. These profiles are registered when a duralumin plate, accelerated to a velocity of 3.5 km/sec, impacts the aforementioned samples. As can be seen, the pressure in the reacting

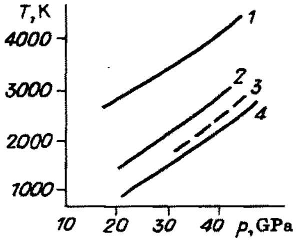

Fig. 7

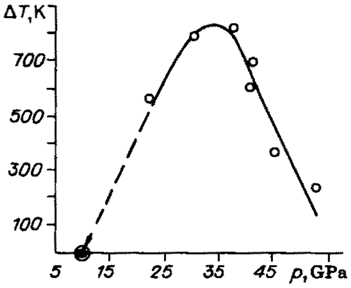

Fig. 8

Fig. 7. Dependences $T(p)$: (1) refers to the completely reacted Sn + S mixture, (2) is the experimental curve for the mixture, (3) refers to sulfur, and (4) to the inert mixture.

Fig. 8. Pressure dependence of the temperature growth due to the exothermal Sn + S reaction; the black dot indicates an extrapolation value of the pressure at the start of reaction.

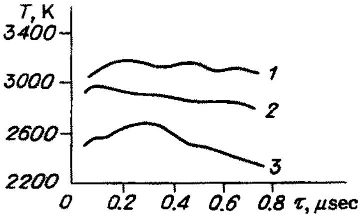

Fig. 9

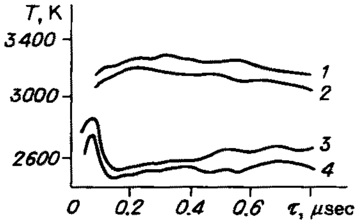

Fig. 10

Fig. 9. Time dependence of brightness temperature of 55% Al + 45% S mixture at $p = 40.3$ (1), 32.2 (2), and 25.7 (3) GPa.

Fig. 10. Time dependence of brightness temperature for 35% Al + 65% S (1, 4) and 55% Al + 45% S (2, 3). (1) and (2) refer to highly-disperse aluminum; (3) and (4) to poorly disperse aluminum.

system is considerably higher than that of the inert substances.

Thus, measurements of the kinematic and thermal characteristics of both the reacting mixtures and the corresponding inert compositions make it possible to assert that chemical reactions of condensed materials under shock compression proceed to a noticeable degree of transformation for a time of $\tau \leqslant 10^{-7}$ sec. To account for this fact, one needs to understand the causes and mechanism of ultrarapid diffusion of atoms in conditions of high dynamic pressures.

MECHANISM OF ULTRARAPID DIFFUSION

As is known from experiments, static compression of solids gives rise to a decrease in mobility of atoms. At the same time, numerous experiments have shown that physical and chemical processes accelerate abruptly if the compression is accompanied by shear deformation. Since strong plastic deformations occur due to shock-wave action, it is natural to expect acceleration of solid-phase reactions. This point of view was first suggested in [41] and is discussed in [4, 5].

Another possible cause of diffusion accelelration was pointed out in [42]: if the shock wave action

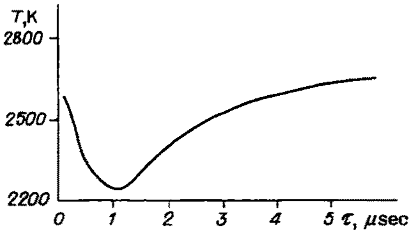

Fig. 11

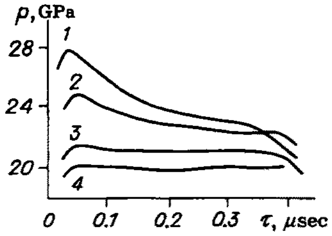

Fig. 12

Fig. 11. Dependence of brightness temperature of Mg + S mixture on time.

Fig. 12. Pressure profiles in 55% Al + 45% S mixture (1, 2), in sulfur (3), and aluminum (4): (1) refers to coarse-grained Al and (2) to fine-grained aluminum.

TABLE 5

Mass Velocities of Tin and Chalcogens

Element	u, mm/μsec at p, GPa				
	10	20	30	40	50
S	1.15	1.95	2.60	3.16	3.67
Te	0.44	0.81	1.13	1.42	1.69
Sn	0.425	0.74	1.01	1.24	1.445

resulted in breakup of a crystal lattice, then the diffusion activation energy could decrease to a value corresponding to a liquid or even to a smaller magnitude.

Another theory that allows one to remove kinetic obstacles hindering diffusion in solids is considered in [43]. If a phase transition of the first kind occurs in the solid under shock loading, then the result of this is breakup of the system of chemical bonds and transformation of atoms in solids into something similar to free radicals. Therefore, according to this hypothesis, at least one of the mixture components must undergo a reconstructive phase transition under given thermodynamic conditions, in order that a solid-phase chemical reaction in the shock wave be accomplished.

The high diffusion rate of atoms in solids under shock loading is attributed in [44–49] to a high concentration of defects, dislocations, and stress gradients, to the chemical affinity of the impurities and the base, and to high temperature.

Thus, the above-listed models attribute the high diffusion rates either to saturation of a solid with defects and its transformation into a quasiliquid or even to its transformation into a conglomerate of free radicals. However, these models are insufficient for explaining the mutual mixing of the mixture components, and sometimes even for explaining the observed diffusion rates. Therefore, there must be an additional mechanism which makes possible the ultrarapid interaction of atoms.

As such a mechanism, [28] suggests a hydrodynamic model of ultrarapid diffusion caused by a difference in the mass velocities of components of a heterogenous mixture. According to this model, complete mixing of the mixture particles occurs when one particle penetrates through another in time $\tau = r/\Delta u$, where r is the size of the link and Δu is the difference in the mass velocities of the mixture components. When $\tau < 10^{-6}$ sec, the reaction influences the Hugoniót curve. If $\tau > 10^{-6}$ sec, it has no influence.

Strictly speaking, one should take as the rate of forced diffusion in a heterogenous mixture not Δu but rather a fraction of this quantity, allowing for the unloading of a stiffer component into a softer one. This fraction is close to 1/2 for most moderate pressures and most of shock adiabats. Consequently, an estimate of the charactereistic diffusion time should be based on the formula $\tau = 2r/\Delta u_{12}$.

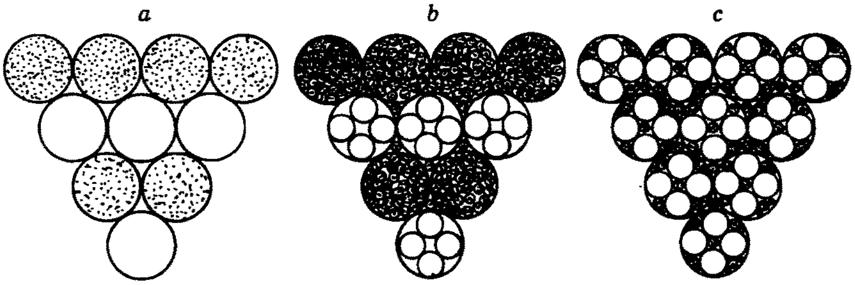

Fig. 13. Mixing mechanism in solid-phase reaction between soft (light) and hard (dark) particles: (a) corresponds to the initial state, (b) to the state in the shock front, and (c) to that behind the shock front.

The mass velocities of the components of a tin–chalcogen system calculated from the known shock adiabats of these elements [2] are presented in Table 5. It is seen that for the particles with a size of 10 μm the above formula yields $\tau = 28$ nsec for the Sn + S mixture, while $\tau = 80$ nsec for Sn + S only at $p = 50$ GPa, which agrees with the experimental data on the threshold values of these reactions.

Although the model suggested correctly conveys the basic pattern of the phenomenon, the question of the mechanism of mutual penetration of particles is still open. An assumption is made in [30] that the shattering which takes place prior to chemical interaction proceeds down to the domain level, i.e., crystal grains with a size of $\sim$ 100 Å [10, 50]; and it is these domains that penetrate one another (Fig. 13), with their surfaces contacting and reacting. In this case, the number of surface atoms amounts to $\sim$ 20% of the total number of atoms in a domain when the bond length of atoms is $\sim$ 3Å. This fits the experimental estimates of the degree of reaction at the first moment of shock compression.

The appearance on the surface of initial grains of chemical compounds whose mechanical properties are different from those of the mixture components leads to a peculiar clearing of the surfaces due to a difference in mass velocities of the grain base and covering, and, as a consequence, to a deeper chemical transformation. As a result of chemical reaction, the size of the grains shattered by the shock wave decreases progressively and can reach a dispersity level that corresponds to an X-ray amorphous state. Such a case was observed in the Ge + Se + Te system [51], where insignificant broadening of X-ray lines was observed due to shock compression of separate components at $T = 93$ K. Loading of the heterogeneous mixture under the same conditions led to an X-ray amorphous product. When the latter was heated up slightly, crystallization of the β-GeSeTe compound occurred and the initial mixture of components was partially extracted.

When the shock adiabats of the mixture components are close, no noticeable shattering or mixing of particles occurs: the reaction proceeds only on the surfaces of the original grains and develops further due to common thermal diffusion. It is precisely this case that is realized in the Mg + S composition, where one observes a progressing chemical interaction of atoms in the post-regime after the passing of the shock wave.

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