Investigation of anomalous compressibility of docosane and cerium under shock-wave action

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Abstract. The behavior of docosane (C₂₂H₄₆) and cerium (Ce) under shock-wave action has been investigated. It was shown that the solid docosane demonstrate elastic-plastic properties and has abnormal compressibility at pressures below 100 MPa. It was found that the strength of docosane remains practically constant and equals to about 24 MPa when passing through the melting point. We determined the shear stress and evolution of compression wave in the area of cerium anomalous compressibility. The value of longitudinal stress at which the γ–α phase transition occurs is also determined. It is shown that the phase transition pressure, under dynamic and static compression coincides and is equal to 0.8 GPa. The spall strength of cerium rises from 0.3 to 0.7 GPa when strain rate increase from 2 \times 10^4 to 1.02 \times 10^6 s⁻¹.

1. Introduction

Adiabatic compressibility of matter (∂V/∂p)₆ is decreasing in most substances with the rise of pressure that means that second derivative is positive:

\[
\left( \frac{\partial^2 V}{\partial p^2} \right)_S > 0.
\]

Inequality (1) is not thermodynamic relation and there may be disturbance of it. In such medium character of pulse propagation is changing principally: rarefaction wave appear as shock wave while compression wave appears as isentropic and its front blurs during its propagation in the sample [1]. Overwhelming majority of mediums has normal compressibility. Only in very rare mediums appears anomalous compressibility. There are several physical reasons leading to it. The example of anomalous compressibility is cerium γ-phase [2–4]. Anomalous compressibility can be observed in all γ-phase area. Specificity of cerium properties is connected with particular qualities of electron shell changing during 4f–5d transition of electrons [4]. Anomalous compressibility of such type leads to blurring of shock-wave front and appearance of rarefaction shock-wave. It is necessary to note that unusual structure of shock waves can be observed for materials with a normal compressibility when phase transition takes a place or under such macroscopic properties as porosity.

Example of unusual behavior of compressibility produced by phase transition is iron. In this case shock wave does not blur but rarefaction shock wave forms. In iron inequality (1) is
fulfilling in every point of phase diagram but the “average” value of derivative (1) is negative [5]. In porosity mediums shock wave front blurs but rarefaction shock wave does not forms due to the collapsing of pours in shock wave which leads to transition to normal compressibility of medium.

Docosane (C_{22}H_{46}) and cerium (Ce) were chosen as objects of the study. In case of cerium the nature of anomalous compressibility is well known and caused by molecular structure [4]. In case of docosane the nature of anomalous compressibility is unknown. The compressibility of saturated hydrocarbons was studied earlier [6, 7] but unusual behavior of docosane under shock compression was observed for the first time in our previous experiments [8].

2. Experimental scheme

Figure 1 shows the schematic diagram of experiments performed to investigate the pulsed compression and tension of the docosane and cerium. Shock waves were created by the impact of aluminium flyer plate \( f \) 0.2–2 mm thick accelerated to 700 m/s by explosive products (EP) with 2 mm thick acrylic plastic shield \( 2 \). Loading conditions were varied by changing flyer plate thickness \( h_i \) and sample \( h_l \) (tables 1 and 2). To measure the velocity, we used a VISAR laser interferometer with a constant of 80.8 m/s, which allowed us to perform measurements at an accuracy of 2 m/s and a time resolution of about 2 ns [9]. A laser beam was reflected from 7 \( \mu \)m thick aluminium foil \( 4 \), which separated the sample from air. The geometric assembly sizes (flat section of the flyer plate was larger than 40 mm) ensured one dimensional loading conditions and excluded the arrival of a lateral unloading wave in the experiment time. When reaching the free surface, the compression pulse had the shape of a triangle, which was determined in specific experiments according to a scheme that was similar to that shown in figure 1a (but a sample was unloaded in water rather than in air). We also used the scheme shown in figure 1b, which allowed us to generate low amplitude (about 0.1 GPa) compression pulses. Shock waves were initiated by an explosive charge \( f \) 20 mm in diameter and 20 g in weight. Than it passes through the acrylic plastic shield \( 2 \), water layer \( 3 \) and acrylic plastic shield \( 4 \), and then comes out to the sample \( 5 \). A laser beam was reflected from 7 \( \mu \)m thick aluminium foil \( 6 \). The shock wave parameters were varied by changing the water layer thickness between the explosive and the sample.

**Figure 1.** Schematic diagrams of the experiments with (a) high and (b) low pressure generators.
3. Experimental results

3.1. Docosane

Figure 2 shows the experimental results for the solid docosane, which represent free surface velocity profiles obtained at an initial temperature of 20°C [10]. The arrival of a shock wave at the free surface causes a jump-like increase in the surface velocity to $W_0$, which is the double mass velocity in the shock wave. A centered rarefaction wave propagates inside the sample; when interacting with the incident unloading wave, it causes internal fracture, spall fracture. During fracture, the breaking tensile stresses are relaxed to zero and form a compression wave. This wave reaches the free surface in the form of a spallation pulse, and its amplitude and the steepness of pulse edge are determined by the relation between the fracture rate and the strain rate in the unloading part of the pulse [11]. As is seen in figure 2, the spallation pulse in the solid docosane is poorly visible; nevertheless, the minimum in the velocity $W_m$ profiles is unambiguously detected. Therefore, we can determine spall strength $P_S$, which characterizes the maximum tensile stresses in the sample, $P_S = 0.5\rho_0 c_0 \Delta W$, where $\Delta W = W_0 - W_m$ [12].

Table 1 gives the obtained spall strengths and the strain rates in the unloading part of the pulse $\dot{\varepsilon} = (dW/dt)/2c_0$. Also in table 1 represents experimental setups parameters and shock wave amplitude $P_0$. Figure 2 shows the velocity profiles for solid docosane at low pressure. At low pressures, tensile stresses were not generated in the sample over the entire recording time and (hence) spall fracture was not observed.

The most interesting result obtained in the experiments on solid docosane is the formation of a two wave configuration, which is not observed only at the maximum pressure (figure 2, curve 1). In all other cases, a precursor is detected before the shock wave front, and its amplitude increases monotonically from zero to the maximum value. The appearance of the precursor is caused by the elastoplastic properties of docosane, and the first wave is elastic. Therefore, the sound velocity is high (2.6 km/s), which was measured by an ultrasonic method and is longitudinal sound velocity $c_l$. Volumetric sound velocity $c_0$ in docosane was taken to be 2.22 km/s (method of its estimation is described below). Therefore, to calculate the spall strength of docosane, we used the formula [13] for an elastoplastic medium $P_S = \rho_0 \frac{c_l c_0}{c_0 + c_l} \Delta W$.

It is seen on the right-hand side of figure 2 that, as the sample thickness increases (i.e., during wave propagation), the elastic precursor duration increases, as it should be for an elastoplastic
Table 1. Docosane. Experimental parameters.

| Number of experiment | hi, mm | hl, mm | P0, MPa | ΔW, m/m | PS, MPa | \(\dot{\varepsilon}\), \(10^4\) s\(^{-1}\) |
|----------------------|--------|--------|---------|---------|---------|-----------------|
| docosane, 20°C, \(\rho_0 = 0.910\) g/cm\(^3\), \(c_0 = 1.46\) km/s |        |        |         |         |         |                 |
| 1(108)              | 2      | 4      | 2250    | 23 ± 1  | 26 ± 1  | 5.0             |
| 2(104)              | 0.4    | 4      | 1102    | 20 ± 1  | 23 ± 1  | 10.8            |
| 3(101)              | 0.4    | 8      | 460     | 21 ± 1  | 24 ± 1  | 9.7             |
| 4(105)              | 0.4    | 16     | 327     |         | —       | —               |
| 5(780)              | EP     | 8      | 191     |         | —       | —               |
| 6(781)              | EP     | 16     | 157     |         | —       | —               |
| docosane, 70°C, \(\rho_0 = 0.777\) g/cm\(^3\), \(c_0 = 1.32\) km/s |        |        |         |         |         |                 |
| 7(725)              | 2      | 8      | 849     | 44 ± 1  | 21.6 ± 0.5 | 3.4             |
| 8(732)              | 0.4    | 2      | 698     | 45 ± 1  | 22.0 ± 0.5 | 5.9             |
| 9(704)              | 0.4    | 2      | 474     | 46 ± 1  | 22.5 ± 0.5 | 9.7             |
| 10(717)             | 0.4    | 8      | 329     | 45 ± 1  | 22.0 ± 0.5 | 7.9             |

body (curves 5, 6). It was unusual that the plastic wave front width increased simultaneously. This smearing of a compression pulse can occur in anomalous compressibility media, where rarefaction shock waves form and compression waves are isentropic. This issue will be discussed in the next section.

Figure 3 depicts the experimental results for liquid docosane. The velocity profiles differ substantially from those of solid docosane. First, a spallation pulse with a steep edge and rather high amplitude is well pronounced. Second, any specific features of the structure of the compression wave front are absent. The spall strength only weakly changed as compared to its value in solid docosane; this is rather unusual, since the strength of a body is considered to decrease in melting.

3.2. Cerium

Table 2 represents experimental parameters and obtained results in experiments with cerium [8]. Figure 3 shows typical velocity profiles obtained in experiments with cerium. Two wave configuration, is clearly seen. It is caused by \(\gamma\)-\(\alpha\) transition. The most interesting observation here is the progressive “blurring” of this configuration during its propagation to a deeper distance within a sample. It is due to the anomalous compressibility of \(\gamma\)-phase Ce that prevents the appearance of shock waves in it and thus results in isentropic character of compression waves passing through it. It should also lead to a shock nature of rarefaction waves in \(\gamma\)-phase, and indeed such a shock rarefaction wave is distinctly observed at the profile 1 in figure 4.

At a pressure lower than the phase transition pressure the two-wave configuration is absent (figure 5). However, the blurring of the compression wave front is still observed. It becomes more distinct with the increase of a sample’s thickness.

Also investigation of the value of spall strength calculated by the formula [13] for an elastoplastic medium \(P_S = \rho_0 \frac{c_0 c_l}{c_0 + c_l} \Delta W\) (where \(c_l = 2.23\) km/s is the longitudinal sound velocity measured with ultrasonic technique) and its dependence on strain rate were made. The results are represented in table 2. Strong dependence between these two values was discovered. Besides it should be noted that very sharp spall pulse is observed. This is related with high value of
4. Discussion of results

4.1. Docosane

The pulsed fracture of docosane above melting temperatures, as the liquids studied earlier, is likely to be caused by the growth of the pores generated by thermal fluctuations [14–18]. This is indirectly indicated by a very weak dependence of the spall strength on the strain rate, which is one of the consequences of the homogeneous nucleation model [19]. This is not obvious for
Table 2. Cerium. Experimental parameters.

| Experiment | $h_i$ | $h_l$ | $P_0$ | $\Delta W$ | $P_S$ | $\dot{\varepsilon}$ |
|------------|-------|-------|-------|------------|-------|-------------------|
| cerium, 20°C, $\rho_0 = 6.75$ g/cm$^3$, $c_0 = 1.68$ km/s | 2(746) | 2 | 4 | 3974 | 41 | 265 | 2.1 |
| 2(64) | 0.4 | 1.5 | 2586 | 106 | 687 | 102 |
| 3(58) | 0.4 | 1.7 | 1354 | 85.5 | 554 | 39.4 |
| 4(57) | 0.4 | 4 | 785 | 64.5 | 417 | 13.3 |
| 5(59) | — | 1.8 | 447 | — | — | — |
| 6(876) | — | 4 | 400 | — | — | — |
| 7(70) | 4 | 1.8 | — | — | — | — |

solid docosane. Nevertheless, the constancy of the spall strength during the passage through the melting temperature suggests that the pore growth mechanism during spallation in this case is also determined by homogeneous nucleation and that the elastoplastic properties of solid docosane do not cause a heterogeneous structure in a sample. The insignificant quantitative change in the spall strength during the passage through the melting temperature is unexpected. In particular, this makes it impossible to determine the state of substance from the temperature evolution of the spall strength. For example, the fact that it is constant in the experiments when the state of substance intersects the melting curve during isentropic unloading after shock compression does not prove the existence of an overheated state in the solid body [20].

Another interesting feature discovered in experiments with docosane is two wave structure, and it is caused by the elastoplastic properties of docosane. In other words, the first wave is an elastic precursor. Moreover, docosane has anomalous compressibility; as a result, compression shock waves cannot form and the pulse front broadens when the pulse moves in a sample, which is visible in figure 3. In this case, compression is isentropic. If the front of the shock wave entering into a sample can be considered as a jump, a centered compression wave should form similarly to the formation of a centered rarefaction wave in normal compressibility media. In figure 6, velocity profiles 5 and 6 are plotted in the $t/h$ coordinates, where $t$ is the time and $h$ is the sample thickness.

It is seen that the velocity profiles almost coincide; that is, the flow is self-similar and the compression wave is indeed centered. As follows from the conditions of conservation of the Riemann invariants [21], the sound velocity should be constant along the characteristics; therefore, they are represented by a pencil of lines. Therefore, we can calculate Lagrangian sound velocity $a_L$ along each characteristic if we know the time of its arrival at the free surface $t_f$, where $c_0$ is the sound velocity at zero pressure:

$$a_L = \frac{h}{t_f + h/c_0}.$$

Since particle velocity $u$, which is half the free surface velocity, is known at every time, we obtain the dependence of $a_L$ on $u$. The calculation result for experiment 5 is shown in figure 6. The sound velocity is seen to decrease sharply with increasing pressure (mass velocity) in the elastic deformation range, and it then decreases slowly according to an almost linear $a_L(u)$ law in the plastic deformation range.

Knowing the dependence of the sound velocity on the particle velocity, we can find a compression isentrope in the pressure $P$–specific volume $V$ plane. To this end, we use the
condition of conservation of the Riemann invariants along the characteristics to derive pressure and specific volume as functions of the particle velocity. Eliminating \( u \), we find isentrope \( P(V) \) (figure 7). This isentrope is seen to have a weak negative curvature, which is most pronounced during the passage from elastic to plastic deformation. The corresponding pressure (Hugoniot limit) is 16 MPa.
4.2. Cerium

As it was shown above two wave configuration of velocity profile of cerium is induced be the phase transition. It is important to note that the transition from $\gamma$ to $\alpha$ phase does not correspond to a certain point on a velocity profile (e.g. the inflection point on profile 1 in figure 4), so it is very difficult to determine with good precision the phase transition pressure from the obtained experimental wave profiles. One of the reasons for that is the re-reflection of the first wave as a result of its circulation between a free surface and a shock wave corresponding to $\alpha$-phase. This leads to the appearance of a smooth second wave instead of the expected shock wave. It is particularly clearly expressed in figure 8. The velocity profile shown there is smoothed due to a circulation of waves. This leads to the disappearance of the salient point corresponding to the phase transition which should be expected on the profile. An approximate location of the salient point can be determined as the intersection point of the extrapolated functions of free surface velocity on time in the regions corresponding to $\gamma$ and $\alpha$ phases. The results of the extrapolation are shown in figure 8 with dashed lines.

Their intersection point gives the position of phase transition as $155\pm5$ m/s. To determine the phase transition pressure, one should take into account the isentropic character of compression in $\gamma$-phase Ce. If the wave front entering a sample can be considered a shock jump, then a centered compression wave should evolve in these conditions in the same way as centered rarefaction waves are formed in materials with normal compressibility. To prove this, the wave profiles 3, 4 shown in figure 4 are redrawn in the $t/h$ coordinates in figure 9 analogous to figure 5 with docosane. It is clearly seen that the velocity profiles coincide with each other up to a certain point where rarefaction waves come. It means that the wave flow is indeed self-similar and a compression wave is indeed centered in this case.

The isentrope of cerium was built analogous to the described-above isentrope of docosane (see figure 10). The dashed line represents the phase transition pressure.

Besides, the dependence of spall strength on strain rate was studied. It was found that as
strain rate increase from $2.1 \times 10^4$ to $1.02 \times 10^6$ s$^{-1}$ the spall strength rises from 0.3 to 0.7 GPa (see table 2).
5. Summary
The behavior of docosane and cerium under shock-wave action was investigated. Despite very different physical properties this two substances demonstrate many similar shock-wave properties. In both substances anomalous compressibility was observed. Different dependences of spall strength on strain rate were revealed. Spall strength does not depend on strain rate in docosane and shows strong dependences in cerium.

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