Research paper

Estimation of shock Hugoniot for unreacted high explosives by various Grüneisen functions

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Abstract

Grüneisen equation of state has been extensively used to describe Shock Hugoniot compression curve for inert materials including unreacted high explosives. In most cases, volume function of the Grüneisen parameter is assumed to be described by very simple functions. In this paper, several volume functions for the Grüneisen parameter have been used to calculate the dependence of shock temperature on the Grüneisen function. The information is important to know the onset temperature and pressure to induce shock to detonation transition of solid phase high explosives. The Grüneisen functions assumed include (i) $\gamma(v) = \text{const}$, (ii) $\gamma(v) = \gamma_0 \cdot (v/v_0)$, (iii) $\gamma(v) = \gamma_0 \cdot (v/v_0)^{1.5}$, (iv) $\gamma(v) = \gamma_{\min}$, and (v) $\gamma(v) = \gamma_0 \cdot (v/v_0)^2$, Here, subscript 0 denotes the value at the uncompressed initial state. The value $\gamma_{\min}$ is the theoretical minimum value of the Grüneisen parameter defined in this paper. Shock Hugoniot function for TMD PETN as well as equation of state function has been calculated based on the hydrostatic isothermal compression data by Olinger et al. Difference in the value of thermal pressure for the above five model functions is more than 2 times. It is striking to note that shock velocity-particle velocity relationship is quite insensitive to the Grüneisen function.

Keywords : Grüneisen type equation of state, Grüneisen parameter, energetic material, static isothermal compression, shock hugoniot

1. Introduction

Shock Hugoniot data have been published for various high energetic materials.[1] They, however, have larger scatter compared with those for inert materials. Reason of this scatter may be attributed to partial reaction and/or decomposition of energetic material under high dynamic pressures and temperatures. Olinger et al[2] have published static isothermal compression data for PETN, and they have calculated shock Hugoniot curve thermodynamically. Static high pressure compression of high energetic material may have less probability of reaction or decomposition with no additional heating during compression process. In this sense, further data by static compression have been published not only for PETN[2,3] but other energetic materials.[4,5] Although high pressure may have the possibility of causing structural phase transition of the material.

Olinger et al's thermodynamic procedure of transforming isothermal data to shock Hugoniot requires value of the specific heat at constant volume and the Grüneisen parameter. Since the compression behavior of both the specific heat and the Grüneisen parameter for high energetic materials are unknown, they had two assumptions. That is, (i) the specific heat at constant volume keeps constant value through isothermal compression and (ii) the Grüneisen parameter divided by specific volume is constant.

Both assumptions are commonly used assumptions in case their experimental values are not available. A treatise in this direction has been published by Sheffield et al.[6] In this paper, a new thermodynamic formulation of transformation from isothermal to shock compression has been developed. We did not assume the assumption (ii), while we also have adopted the assumption (i). By these

analyses, we would like to discuss the contribution of the functional form of the Grüneisen parameter to the estimated shock Hugoniot curve. Numerical examples of Hugoniot curve for PETN have been given and the contribution of the Grüneisen parameter has been discussed.

Researches conducted in this paper has been made to obtain equation of state (EOS) to implement to the numerical code for the detonation phenomena simulation.

2. Thermodynamics of isothermal compression curve and shock Hugoniot curve for energetic materials

2.1 Grüneisen type equation of state

At first, we assume that the EOS for reactants can be described by the Grüneisen type equation of state.[7),8)]

$$p = f(v) + \frac{\gamma(v)}{v}\varepsilon, \tag{1}$$

where p, v, γ, and ε denote the pressure, the specific volume, the Grüneisen parameter and the specific internal energy, respectively. In this equation, the Grüneisen parameter is assumed to be a function only of volume.

Nagayama[7)] has derived two new thermal variables, $C(S)$ and $\Theta(v)$ based on the volume-dependent Grüneisen parameter. In this case, thermal internal energy can be written as

$$\varepsilon_T(v,S) = C(S)\cdot\Theta(v), \tag{2}$$

where the volume function $\Theta(v)$ is given by

$$\Theta(v) = \Theta(v_0)\exp\left[-\int_{v_0}^{v}\frac{\gamma(v)}{v}dv\right] \tag{3}$$

where suffix 0 denotes the value at a reference state, such as the initial state. Entropic functions $C(S)$ and $\Theta(v)$ are found to be conjugate with each other as two new thermal variables. This is demonstrated by the following equation, which shows that these new thermal variables are related to temperature and entropy as

$$T\cdot dS = \Theta(v)\cdot dC(S) \tag{4}$$

We call the volume function $\Theta(v)$ the characteristic temperature because it serves as the integrating denominator in Equation (4), and corresponds to the Debye temperature if one assumes the Debye model for specific heat. Differentiation of specific internal energy, Equation (2) with specific volume along an isentrope gives the pressure.

$$p = -\left(\frac{\partial\varepsilon}{\partial v}\right)_S = p_c(v) + \frac{\gamma(v)}{v}C(S)\cdot\Theta(v), \tag{5}$$

where suffix c denotes cold component of pressure. These considerations have been published elsewhere.[8)]

A thermodynamic identity including temperature, entropy and the Grüneisen parameter gives further constraint on the relationship between the Grüneisen parameter and other variables.

$$\frac{dT}{T} = -\frac{\gamma(v)}{v}dv + \frac{dS}{C_v} \tag{6}$$

or by using the definition of characteristic temperature, i. e., Equation (3), Equation (6) is given in another form

$$\frac{dT}{T} = \frac{d\Theta}{\Theta} + \frac{dS}{C_v} \tag{7}$$

Since lhs of Equation (7) is a total differential, the assumption of the Grüneisen parameter being a function only of volume, leads to the result that specific heat at constant volume should be a function only of entropy. Debye model for the specific heat with one Debye temperature, for example, is compatible with this rule. Or at least one may say mathematically that arbitrary volume functions of the Grüneisen parameter and arbitrary entropy function of the specific heat is compatible with each other.

2.2 Fundamental equations for deriving shock Hugoniot curve based on isothermal compression data

Interconnection between shock Hugoniot pressure and isothermal pressure with the same specific volume is given by

$$p_H - p_t = \frac{\gamma(v)}{v}[\varepsilon_H - \varepsilon_t] \tag{8}$$

where suffices H and t denote quantities on Hugoniot and on an isotherm. Differential of Equation (8) is written as

$$\begin{aligned} dp_H - dp_t &= \frac{\gamma(v)}{v}[d\varepsilon_H - d\varepsilon_t] + [\varepsilon_H - \varepsilon_t]\frac{d}{dv}\left[\frac{\gamma(v)}{v}\right]dv \\ &= \frac{\gamma(v)}{v}[d\varepsilon_H - d\varepsilon_t] + \frac{v}{\gamma(v)}[p_H - p_t]\frac{d}{dv}\left[\frac{\gamma(v)}{v}\right]dv \end{aligned} \tag{9}$$

Differentiation of the Rankine-Hugoniot relation gives

$$d\varepsilon_H = -\frac{1}{2}(p_H + p_0)\,dv + \frac{1}{2}(v_0 - v)\,dp_H. \tag{10}$$

While the change in internal energy along an isothermal compression curve can be

$$d\varepsilon_t = \left[\frac{\gamma(v)}{v}C_v T - p_t\right]dv. \tag{11}$$

Applying Equation (10) and (11) to Equation (9) gives

$$\begin{aligned} dp_H - dp_t = \frac{\gamma(v)}{v}&\left[-\frac{1}{2}(p_H + p_0)\,dv + \frac{1}{2}(v_0 - v)\,dp_H - \left[\frac{\gamma(v)}{v}C_v T - p_t\right]dv\right] \\ &+ \frac{v}{\gamma(v)}[p_H - p_t]\frac{d}{dv}\left[\frac{\gamma(v)}{v}\right]dv \end{aligned} \tag{12}$$

Rearranging terms of Equation (12), we obtain

$$\begin{aligned} \frac{dp_H}{dv} = &\left[\frac{d_t}{dv} - \frac{\gamma(v)}{v}\left\{\frac{p_H + p_0}{2} - p_t\right\} - \left(\frac{\gamma(v)}{v}\right)^2 C_v T + [p_H p_t]\frac{d}{dv}\left(\ln\left(\frac{\gamma(v)}{v}\right)\right)\right] \\ &\Big/\left[1 - \frac{\gamma(v)}{v}\frac{v_0 - v}{2}\right] \end{aligned} \tag{13}$$

By giving the isothermal compression curve data, $p_t(v,T_0)$, the specific heat, C_v, and the Grüneisen function, $\gamma(v)$, Equation (13) can be integrated over volume to obtain shock Hugoniot pressure. It is apparent that

Equation (13) is considered to be equivalent to Equation (17) in Olinger et al's paper in 1975.[2] By adopting Equation (13) instead of Olinger et al's formula, one may at least choose physical model for the specific heat other than using the constant C_v model. It is also noted that the Grüneisen function other than $\rho\gamma = \text{const}$ model can be used both Equation (13) and Olinger formula.

3. Equation of state for unreacted energetic material based on the isothermal compression data

Figure 1 shows the schematic illustration of an isotherm, an isentrope and shock Hugoniot on $p-v$ plane. Isotherm and isentrope are the one centering uncompressed initial state. Starting from the isothermal compression curve, we will estimate both the state variables on the isentrope and those on shock Hugoniot based on the specific heat constant model. More specifically, we can establish the relationship between isothermal pressure, isentropic pressure and Hugoniot pressure with the same specific volume as shown by three dot points in Figure 1.

Shock pressure p_H has to be determined by the integration of Equation (13) based on the information on the isothermal compression curve, $p_t(v,T_0)$. Thermal variables on shock Hugoniot states can be obtained relatively easy, provided that $C_v = \text{const}$. Pressure difference between Hugoniot pressure and isothermal pressure with the same specific volume can be estimated by the formula

$$dp = \frac{\gamma(v)}{v} C_v dT \text{ with } dv = 0 \tag{14}$$

Integrating Equation (14) between the state on an isotherm to the state on the Hugoniot along an isochoric, we have

$$p_H - p_t = \frac{\gamma(v)}{v} C_v [T_H - T_0] \tag{15}$$

As shown later, this equation can be used to determine shock temperature.

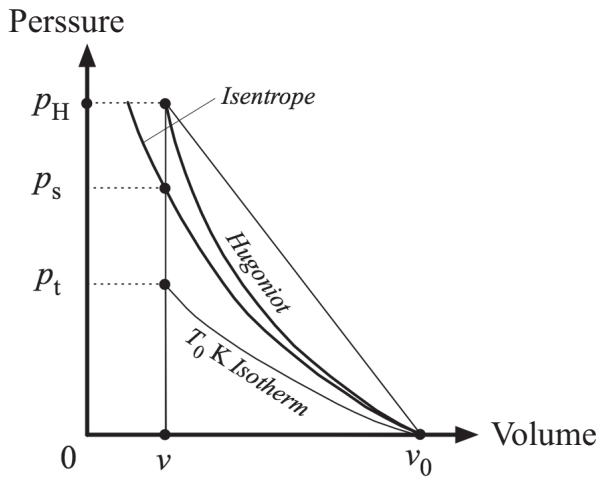

Figure 1 Isotherm, Isentrope and Hugoniot on $p-v$ plane. Three Pressure values, p_H, p_s and p_t are with the same specific volume v.

4. Test functions of the Grüneisen parameter

Almost all of the analyses above is based on the information on the volume-dependent Grüneisen parameter. Previous attempts on the studies of shock Huginot have been made by using the assumption that $\gamma(v)/v = \gamma_0/v_0 = \text{const}$. Since no serious evidences have been found whether this assumption is valid or not, we have tried to use several test functions in order to see its contribution to the calculated shock Hugoniot from known isotherm. We have used following five Grüneisen functions, i.e.,

$$\text{(i)} \quad \gamma(v) = \gamma_0 = \text{const}, \tag{16}$$

$$\text{(ii)} \quad \gamma(v) = \gamma_0\left(\frac{v}{v_0}\right), \tag{17}$$

$$\text{(iii)} \quad \gamma(v) = (v_{v_0})^{1.5}, \tag{18}$$

$$\text{(iv)} \quad \gamma(v) = \gamma_0\left(\frac{v}{v_0}\right) \Big/ \left\{\gamma_0\left(1-\frac{v}{v_0}\right)+1\right\}, \tag{19}$$

$$\text{(v)} \quad \gamma(v) = \gamma_0\left(\frac{v}{v_0}\right)^2. \tag{20}$$

Rate of decrease in γ with compression is larger for lower row of these functions. We have added one specific function, Equation (19) by the following reason. First two functions have been well used previously. Third and fifth functions have also been used by high-pressure scientists to provide possibilities of faster decrease in Grüneisen parameter by compression. Value of the fourth Grüneisen parameter calculated by Equation (19) is found to be the possible minimum value due to the following reason. One of fundamental features of shock wave propagation is

$$a_H + u_p > u_s \tag{21}$$

where a_H, u_s and u_p denote the local sound velocity behind the shock front, the shock front propagation velocity and the particle velocity, respectively. Equation (21) means that shock velocity is subsonic behind shock front.[9] Along shock Hugoniot, both shock velocity and particle velocity increases with shock strength, and Equation (21) shows that sound velocity will also increase. Most of the shock Hugoniot has the density limit, and with increasing shock strength, shock and particle velocity increases without limit. This is due to extreme high temperature attained by shock compression. In this sense, similar increase in sound velocity with higher temperature will be explained by the positive contribution of the thermal component of sound velocity. This condition for the Grüneisen EOS leads to the conclusion that Grüneisen parameter must have the possible maximum value for each specific volume. Concrete functional form for this limiting value is given by Equation (19). At some interval of specific volume, value of the Grüneisen parameter of case (v) is smaller than that of case (iv). We must say that in such volume interval, case (v) is unphysical. We still add the case (v) only for comparison.

Characteristic temperature function defined by Equation (3) for five test functions has been given as

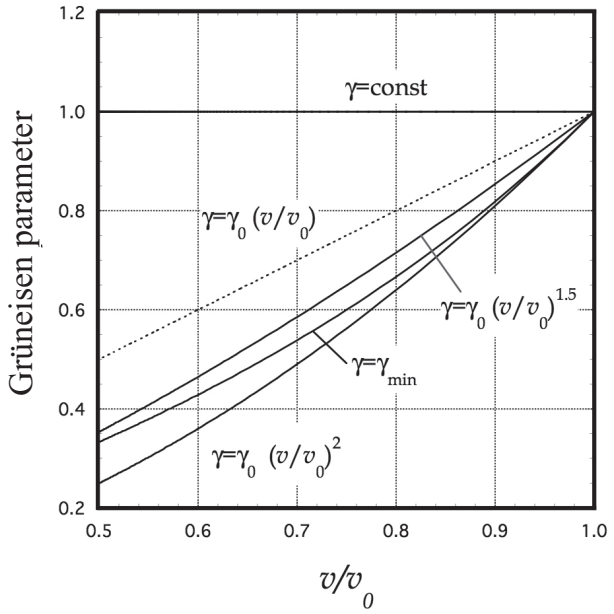

Figure 2 Assumed Grüneisen parameter as a function of specific volume.

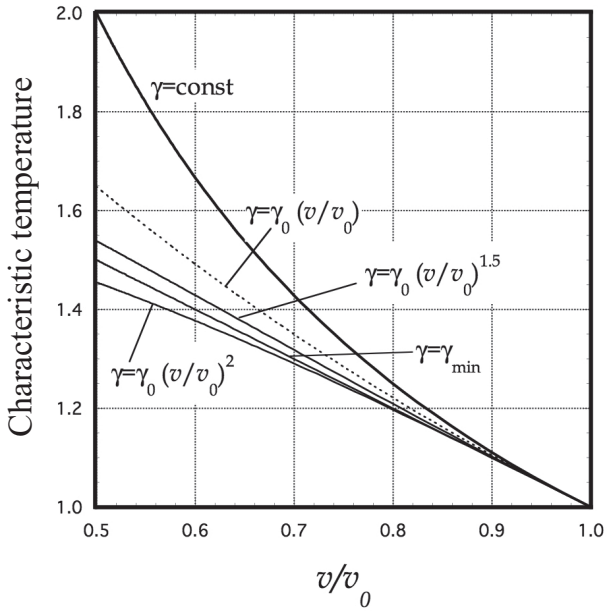

Figure 3 Characteristic temperature function corresponding to the assumed Grüneisen parameter in Figure 2.

$$\text{(i)}\quad \Theta(v)=\Theta(v_0)\left(\frac{v}{v_0}\right)^{-\gamma_0} \tag{22}$$

$$\text{(ii)}\quad \Theta(v)=\Theta(v_0)\exp\left[+\gamma_0\left(1-\frac{v}{v_0}\right)\right] \tag{23}$$

$$\text{(iii)}\quad \Theta(v)=\Theta(v_0)\exp\left[+\frac{\gamma_0}{1.5}\left[1-\left(\frac{v}{v_0}\right)^{1.5}\right]\right] \tag{24}$$

$$\text{(iv)}\quad \Theta(v)=\Theta(v_0)\left[+\gamma_0\left(1-\frac{v}{v_0}\right)+1\right] \tag{25}$$

$$\text{(v)}\quad \Theta(v)=\Theta(v_0)\exp\left[+\frac{\gamma_0}{2}\left[1-\left(\frac{v}{v_0}\right)^{2}\right]\right] \tag{26}$$

Equations (22)-(26) can be used to establish isentrope and shock Hugoniot functions for energetic materials.

Figures 2 and 3 shows representations of the Grüneisen functions assumed and their corresponding characteristic temperature functions. As shown in Figure 2, decrease in Grüneisen parameter with compression will increase with the order as in Equation (16)-(20). Increase in the corresponding characteristic temperature with compression will decrease with the same order of Equation (22)-(26). Grüneisen function given by Equation (26) gives lower value compared with the lowest possible value by Equation (25). This function is chosen to represent only for comparison with other functions.

5. Calculations for PETN shock Hugoniot

5.1 Pressure-volume shock Hugoniot and Grüneisen equation of state for PETN

Two data sets for TMD PETN isothermal compression data have been available by Olinger et al[2] and by Yoo et al.[3] Figure 4 shows these two kinds of data. Due to some scatter of the data, least square fit by a polynomial expression is also plotted in this figure. The polynomial

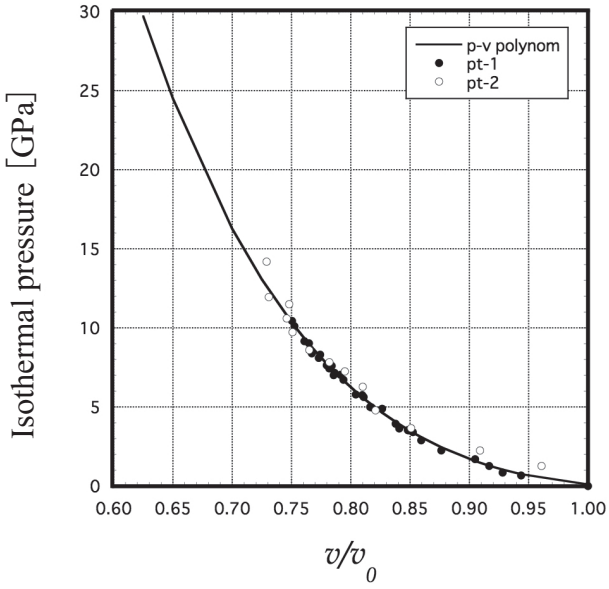

Figure 4 Isothermal compression data of Olinger et al[2] (solid circles) and Yoo et al[3] (open circles) and its least square fit.

expression determined is given by

$$p_t = 1394.8-5588.1\left(\frac{v}{v_0}\right)+8512.2\left(\frac{v}{v_0}\right)^2-5830.5\left(\frac{v}{v_0}\right)^3 +1511.6\left(\frac{v}{v_0}\right)^4 \tag{27}$$

A solid line in Figure 4 shows this polynomial, and it is extended to the pressure region over the data area. Sometimes, isothermal compression curves are fit by the Murnaghan[10] or Birch-Murnaghan[11] equation of state. In such cases, bulk modulus or derivative of bulk modulus is estimated as parameters of these equation of state.

We have calculated shock Hugoniot and an isentrope centering uncompressed state based on these two data sets by integrating Equation (13) using polynomial formula, Equation (27) for isothermal compression.

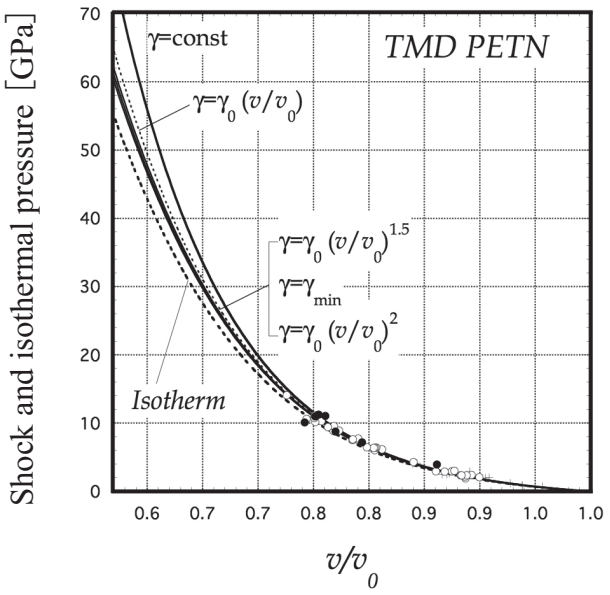

Figure 5 Shock Hugoniot compression curve for TMD PETN calculated by isothermal data together with assumed Grüneisen functions. Estimated $p-v$ shock Hugoniot points are also plotted by published U_s-U_p Hugoniot data.

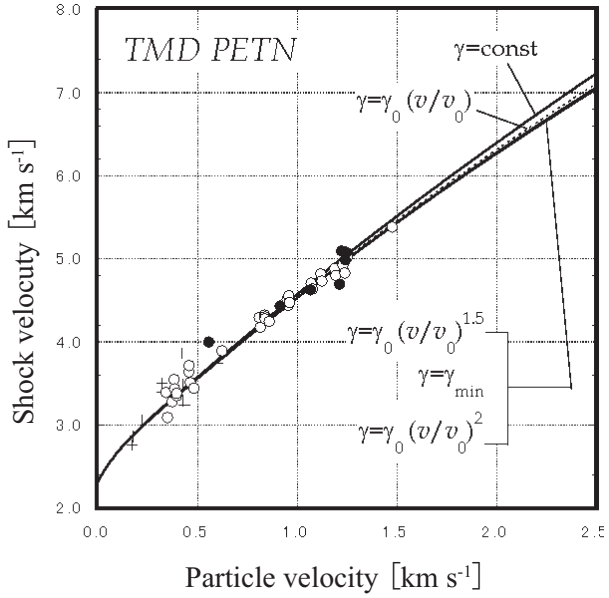

Figure 6 Estimated shock velocity - particle velocity Hugoniot for PETN.
Three kinds of symbols are published shock Hugoniot data[1] for crystalline PETN.

According to Equation (13), one also needs the volume derivative of Equation (27). The expression of derivative is calculated directly from Equation (27). Estimated shock Hugoniot compression curve depends on the assumed Grüneisen functions, and is depicted in Figure 5. The figure also contains Hugoniot points calculated by published Hugoniot data.[1] The most large difference between isothermal compression curve and shock Hugoniot is seen in the case of $\gamma=$ const, i.e., Equation (16). The difference is seen to decrease with cited order as in Equation (16)-(20). This difference naturally is attributed to the thermal pressure added through irreversible heating by shock compression.

From Figure 5, one may see that (i) $\gamma(v)=$ const gives highest shock pressure with the same specific volume. Difference in pressure between the cases, (iii), (iv) and (v) is found to be very small.

It is possible to calculate shock velocity-particle velocity Hugoniot from calculated pressure-volume Hugoniot. Bulk sound velocity at uncompressed state can be calculated as follows: One may first calculate the difference in isentropic pressure and an isotherm along an isochoric in Equation (14) as

$$p_s-p_t=\frac{\gamma(v)}{v}C_v[T_S-T_0]=\frac{\gamma(v)}{v}C_vT_0\left[\frac{\Theta(v)}{\Theta_0}-1\right] \tag{28}$$

The last expression has been reached by using the formula

$$T_S=T_0\frac{\Theta(v)}{\Theta_0}=T_0\exp\left[-\int_{v_0}^{v}\frac{\gamma(v)}{v}dv\right] \tag{29}$$

which is obtained by integrating Equation (7) with $dS=0$. By differentiating Equation (28) by volume, we have

$$\left.\frac{dp_s}{dv}\right|_0=\left.\frac{dp_t}{dv}\right|_0-\left(\frac{\gamma_0}{v_0}\right)^2C_vT_0 \tag{30}$$

From this equation, estimated bulk sound velocity at the initial state is given by

$$c_b^2=-v_0^2\left.\frac{dp_s}{dv}\right|_0=-v_0^2\left.\frac{dp_t}{dv}\right|_0+\gamma_0^2C_vT_0 \tag{31}$$

which gives the velocity of 2.313 km·s^{-1} irrespective of Grüneisen functions.

Estimated U_s-U_p Hugoniot for each Grüneisen function is shown in Figure 6.

In this figure, published shock Hugoniot data[1] for crystalline PETN of initial density of 1.773-1.778 g·cm^{-3} are also shown. Data are seen to be scattered around present calculations. One may see from this figure that dependence of U_s-U_p Hugoniot on the functional form of the Grüneisen parameter is quite small compared with that in p_H-v/v_0 Hugoniot. In other words, it is very difficult to obtain information on the Grüneisen parameter by the measurement of the Hugoniot data. One may note, however, that our calculation does not include the rigidity effects, so that U_s-U_p Hugoniot will change slightly. Even so, insensitivity of U_s-U_p Hugoniot to the functional form of the Grüneisen parameter remains valid, if one includes rigidity effects.

We will rewrite Equation (1) to the following form.

$$p=F(v)+\frac{\gamma(v)}{v}[\varepsilon-\varepsilon_0] \tag{32}$$

where the material function $F(v)$ can be rewritten as

$$\begin{aligned}F(v)&=p_H(v)-\frac{\gamma(v)}{v}[\varepsilon_H(v)-\varepsilon_0]\\&=p_H-\frac{\gamma(v)}{v}\frac{p_H(v)}{2}(v_0-v).\end{aligned} \tag{33}$$

Three kinds of equations, i.e., (i) assumed Grüneisen functions, Equation (16)-(20), (ii) calculated Hugoniot pressure function, $p_H(v)$, and (iii) the material function $F(v)$ given by Equation (33) determines the functionl

form of the Grüneisen equation of state, i.e., Equation (32).

From Figure 5 and Figure 6, one finds relatively large scatter in shock data which may be attributed to partial reaction at the shock front. Even so, on average, difference between shock data and theoretical prediction is relatively small. Therefore, theoretical approach which is not based on shock experiments seems more preferable to provide reasonable EOS at least for numerical simulation purposes.

5.2 Estimation of shock temperature for PETN

Shock temperature as a function of volume can be calculated by using Equation (15). Figure 7 shows estimated temperature for various Grüneisen functions. Tendency of the magnitude of shock temperature with various Grüneisen function is seen to be similar to that of shock pressure.

In order to see the estimated temperature more in detail, compression ratio of around $v/v_0 = 0.6$ is magnified and depicted in Figure 8. One may see still very large difference in shock temperature depending on the Grüneisen function. In this figure, difference in pressure between the cases, (iv) and (v) is found to be very small.

6. Summary

In this paper, Grüneisen equation of state has been established to describe Shock Hugoniot compression curve for unreacted high explosives. Main purpose of the formulation is to give insight into the contribution of the volume dependence of the Grüneisen parameter. Although the volume function of the Grüneisen parameter has been assumed to be described by very simple functions. In this paper, several volume functions for the Grüneisen parameter have been used to calculate the dependence of shock Hugoniot temperature on the Grüneisen function. The information is important to know the onset temperature and pressure to induce shock to detonation transition of solid phase high explosives. A numerical procedure is derived to compute shock Hugoniot and high pressure isentrope by using the Olinger et al's isothermal compression data for PETN. Further thermodynamic formulation was required not only for the Grüneisen function but the constant specific heat.

From the calculation for PETN, one may say, at least that $U_s - U_p$ Hugoniot is quite insensitive for the functional form of the Grüneisen parameter. On the contrary, difference on thermal pressure or temperature strongly depends on the Grüneisen function.

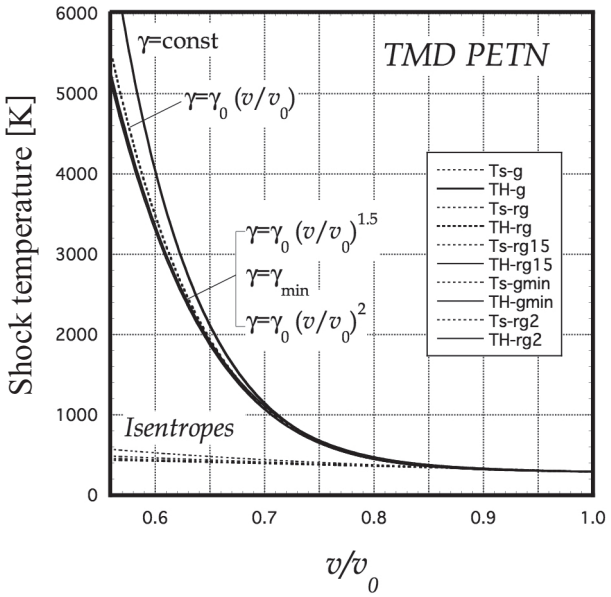

Figure 7 Shock temperature for PETN calculated by Equation (15) with assumed Grüneisen functions.

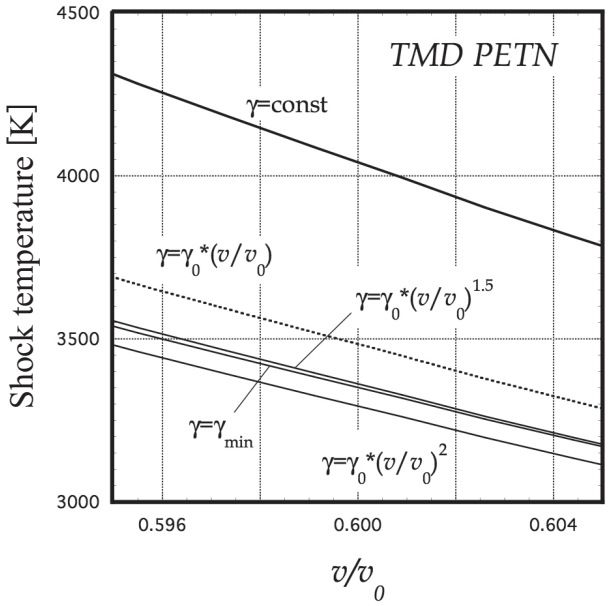

Figure 8 Detailed comparison of estimated shock temperature for PETN with assumed Grüneisen functions.

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