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Abstract

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ON MELTING UNDER COMPRESSION BY A SHOCK WAVE

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When compressed by strong shock waves, a substance is heated to very high temperatures, of the order of several tens of thousands of degrees. This is especially characteristic for the compression of porous substances, when, at a density close to normal, temperatures are reached that substantially exceed the normal melting temperature [1]. Therefore, the form of the shock adiabat that intersects the melting curve of the substance is of interest.

1. The law of conservation of energy of a substance for a shock wave has the form

$$\frac{P-P_0}{2}(V+V_0)=H-H_0, \tag{1}$$

where P, V, H and P_0, V_0, H_0 are the pressure, volume, and enthalpy, respectively, behind the wave front and before it.

When a first-order phase transition has partially occurred behind the shock-wave front, the enthalpy can be written [2] in the form

$$H=H_{\mathrm{t}}+\lambda L, \tag{2}$$

where H_{t} is the enthalpy of the solid phase on the melting curve at pressure P; λ is the fraction of the liquid phase, and L is the heat of fusion at pressure P.

Denoting the volumes of the solid and liquid phases on the melting curve at pressure P by V_{t} and V_{l}, and $\Delta V=V_{\mathrm{l}}-V_{\mathrm{t}}$, one may write $\lambda=(V-V_{\mathrm{t}})/\Delta V$. Taking into account the Clapeyron-Clausius equation $dP/dT=L/T\Delta V$, equation (2) is rewritten in the form

$$H=H_{\mathrm{t}}+(V-V_{\mathrm{t}})\,T\frac{dP}{dT}, \tag{3}$$

where T is the temperature.

It follows from (3) that the shock adiabat in the region of phase coexistence is determined only by the equation of state of the solid phase and by the melting curve. Thus, when considering the question of the influence of melting on the shape of the shock adiabat, information on the liquid phase is not needed.

Differentiating equation (1) with respect to P, taking (3) into account, we find the slope of the shock adiabat in the region of phase coexistence:

$$\left(\frac{\partial P}{\partial V}\right)_{\Gamma}^{\phi} = \frac{dP}{dT}\left(\frac{P-P_0}{2} - T\frac{dP}{dT}\right)\left\{\left(\frac{\partial E}{\partial T}\right)_V - T\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial P}\right)_T + (V-V_{\mathrm{t}})T\frac{d^2P}{dT^2} + \right.$$

$$\left. + \frac{dP}{dT}\left[2T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T - T\frac{dP}{dT}\left(\frac{\partial V}{\partial P}\right)_T - \frac{V_0-V_{\mathrm{t}}}{2}\right]\right\}^{-1}, \qquad (4)$$

where E is the internal energy.

All values of the partial derivatives in (4) are taken from the equation of state of the solid phase on the melting curve at pressure P. The total derivatives refer to the melting curve.

The slope of the shock adiabat outside the coexistence region has the form

$$\left(\frac{\partial P}{\partial V}\right)_{\Gamma} = \frac{\left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{\partial P}{\partial E}\right)_V\left[T\left(\frac{\partial P}{\partial T}\right)_V - \frac{P-P_0}{2}\right]}{1 - \frac{V_0-V}{2}\left(\frac{\partial P}{\partial E}\right)_V}. \qquad (5)$$

It is known that for most metals $\Delta V > 0$ and the slope of the melting curve is positive, $\partial P/\partial T > 0$. Comparing (4) and (5), we see that in this case $(\partial P/\partial V)_{\Gamma}^{\phi}$ may be either greater or smaller than $(\partial P/\partial V)_{\Gamma}^{-}$, depending on the magnitude of dP/dT. However, the isentropic compressibility of a substance in the coexistence region, in accordance with Le Chatelier' s principle, is always greater than the compressibility of an individual phase.

At present there is a satisfactory theory of the equation of state of the solid phase and abundant experimental material for determining its parameters. Therefore, to find the melting curve $T_{\mathrm{m}} = T(P)$, assumptions are needed either about the equation of state of the liquid phase or about the relation between the melting temperature and the volume. In the present work the latter case is considered.

2. Assuming that melting of a substance occurs when the amplitude of atomic vibrations in the crystal lattice of a solid reaches a certain fraction of the interatomic distance, Lindemann (3) obtained the relation

$$RT = AV^2\frac{d^2E_x}{dV^2}, \qquad (6)$$

where R is the gas constant, and E_x is the elastic energy of interaction of atoms. Gilvarry (^{4}), generalizing Lindemann' s law (6) to the case of high pressures, found that the values of the constant A may differ somewhat for different substances.

It is possible to find the melting curve in another way as well. From the parameters characteristic of melting, let us form the dimensionless quantity

$$\frac{LV_T}{RT\Delta V} = a. \tag{7}$$

Table 1

	Al	Cu	Pb	Ni
ρ_0, g/cm^3	2.71	8.93	11.34	8.90
ρ_{exp}, g/cm^3	2.57	8.38	11.00	8.27
ρ_{calc}, g/cm^3	2.566	8.401	11.000	8.200
$A \cdot 10^2$	1.301	1.426	2.265	1.570
a	19.7	19.4	32.0	19.9

Kubaschewski (^{5}) showed that the values of a, calculated from experimental data on melting at $P = 0$, are close in order of magnitude for many metals. This fact allows one to hope that the quantity a will not change strongly along the melting curve.

The melting curve is found by integrating the Clapeyron–Clausius equation with allowance for equation (7) and the equation of state of the solid phase.

3. Let us use the equation of state of metals in the solid phase in the form

$$F = E_x(v) - 3RT \ln \frac{T}{\theta(V)} - 0.5\beta(V)T^2, \tag{8}$$

where

$$\theta(V) = \text{const} \cdot V^{2/3} \left(\frac{d^2 E_x}{dV^2} \right)^{1/2}.$$

The last term in (8) describes the free energy of the electrons. The functions $E_x(V)$ and $\beta(V)$ in the present work were taken from (^{1}). The density of a solid metal at the melting temperature and $P = 0$, calculated from this equation of state, agrees well, as is seen from Table 1, with experimenfurther, which confirms the validity of the equation of state (8) up to the melting temperature. From the known experimental data on melting it is easy to find the values of the constants A and a in (6) and (7). These values are given in Table 1.

Calculation of the melting curves by (6) showed that the slope dP/dT at $P = 0$ is greater than the experimental value $^{(6-8)}$ by 30% for Al, Cu, and Ni, and smaller by 20% for Pb. The indicated difference is substantial and may lead at high pressures to large errors.

Table 2

		Al	Cu	Pb	Ni
Solid substances	**Solid substances**	**Solid substances**	**Solid substances**	**Solid substances**	**Solid substances**
According to equation (6)	$P \cdot 10^{-6}$, bar	1.15	2.54	0.5	7.4
According to equation (6)	$T \cdot 10^{-3}$, °K	4.0	7.0	2.6	14.0
According to equation (7)	$P \cdot 10^{-6}$, bar	2.35	4.3	0.73	–
According to equation (7)	$T \cdot 10^{-3}$, °K	10.5	14.5	4.3	–
Porous substances	**Porous substances**	**Porosity**	**Porosity**	**Porosity**	**Porosity**
		1.43	1.57	1.2	1.43
According to equation (6)	$P \cdot 10^{-6}$, bar	0.14	0.2	0.13	0.73
According to equation (6)	$T \cdot 10^{-3}$, °K	1.5	2.0	1.3	3.7

		Al	Cu	Pb	Ni
According to equation (7)	$P \cdot 10^{-6}$, bar	0.18	0.24	0.15	2.33
According to equation (7)	$T \cdot 10^{-3}$, °K	1.9	2.4	1.5	9.6

The initial slope of the melting curves by the second method is determined by the choice of the constant a in condition (7). The curves obtained have a noticeably smaller curvature than the curves according to (6). This can be seen from Table 2, where the temperatures and pressures on the melting curves according to equations (6) and (7) are presented at the point of intersection of the latter with the shock adiabats of metals with two different initial densities (1). The table shows that the melting pressure under shock compression depends strongly on the form of the melting curve, especially for solid substances.

It follows from the calculation that for the melting curves, both according to (6) and according to (7),

$$\left|\left(\frac{\partial P}{\partial V}\right)_r^{\phi}\right| > \left|\left(\frac{\partial P}{\partial V}\right)_r\right|.$$

This indicates that the melting process cannot cause the appearance, in the metals under consideration, of a second shock wave. The changes in the slope of the shock adiabats of solid metals upon entering the region of coexistence of the solid and liquid phases, calculated with allowance for (6), amount to 30% for Pb and Al, 50% for Cu, and 90% for Ni. The same jumps in slope, calculated with allowance for (7), amount to 30, 120, and 160% for Pb, Al, and Cu, respectively. The published experimental data on shock compression of metals (2,9,10) do not make it possible to state with confidence that there are no jumps in the slope of the shock adiabats. However, jumps of the magnitudes given above, especially of the order of 100%, are unlikely to occur, unless one assumes a very strong decrease of ΔV with pressure.

Estimates were made of the influence of melting on the sound velocity behind the shock-wave front. For the melting curves according to (6), the decrease in the sound velocity amounts to 2% for Pb, Al, and Cu and 6% for Ni; for the melting curves according to (7), 5% for Pb and 8% for Al and Cu. Jumps of magnitude $2 \div 5\%$ are within the pre-

within the limits of the accuracy of the experiment on measuring the sound velocity behind the shock-wave front in Al, Cu, and Pb (11). The location of the jump for Al and Cu according to (7) lies outside the experimentally investigated region.

If the slope of the melting curve at its point of intersection with the shock adiabat is greater than that of the curve according to (6), then the jumps in the slope of the shock adiabat and in the sound velocity become substantially smaller and are hardly reflected at all in the form of the shock adiabat.

The estimates carried out show that, by careful mechanical measurements of shock waves, it is possible to determine the point of intersection of the shock adiabat and the melting curve, provided the slope of the latter is not too large.

The paper touched upon the question of the time characteristic of the melting process in a shock wave. The calculations were carried out under the assumption that thermodynamic equilibrium is established behind the wave front.

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Note: Figure translations are in progress. See original paper for figures.

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