

SCOPE FOR PRODUCING SUPERCOOLED MELTS
BY A DYNAMIC METHOD

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There are various ways of making supercooled melts by rapid cooling [1, 2]. The substance is transferred to a temperature range well below the melting point T_m , where crystallization is retarded by the high viscosity. By increasing the cooling rate in the supercooling appropriately, one can attain a finely crystalline or amorphous state for any material [1]. High cooling rates are attained in all the methods by using small thicknesses of molten metal in contact with a cold substrate.

An essentially different way of obtaining supercooled states is to melt the material at a shock-wave front and cool it in the decompression wave behind it. The cooling rate in that case can be as high as 10^{10} °K/sec [3], which is above the record levels attained in traditional methods. However, the course of the isentropic curves and melting ones for some materials is such that the substance melting at the shock-wave front remains liquid on decompression [4, 5]. Therefore, the use of dynamic pressures to produce supercooled states amounts virtually to the preparation of thin layers [3, 6]. The high cooling rates in these are produced on account of the small thicknesses, as in traditional methods.

However, there exists a class of materials where the advantages of dynamic loading can be used more fully under certain conditions; these are substances in which the form of the melting curve is anomalous, i.e., the melting point falls in a certain pressure range (Fig. 1). It is readily seen that if the material is melted by the shock wave near the triple point A, then on decompression along the curve AB it is in the supercooled state, because the melting point rises as the pressure falls (even without allowance for cooling in the decompression wave).

It is assumed that crystallization does not occur during the fall in pressure. The supercoolings ($T_m - T_{min}$) thereby attained may be as much as 150-700°K (Table 1). These data have been taken from [7, 8]. For liquid Ge purified from impurities, a maximum supercooling of 227°K has been attained [1], i.e., less by about a factor 2 than the quantity attained in the proposed process. If the width of the decompression wave is about 10^{-7} sec, then the effective cooling rates will be in the range 10^9 - 10^{10} °K/sec. High cooling rates are observed below T_m , i.e., the material is transferred to the supercooled state without passing through the high-temperature range $T_m - T_b$, where the crystallization may occur rapidly. Therefore, here, instead of cooling from T_m to T_b by heat transfer, we have a process of pressure reduction. The supercooling can be attained in the decompression wave with a material having a normal course for the melting curve only because of nonequilibrium melting.

The scope for melting a material in the bulk of a shock wave with a pressure close to p_{min} is far from obvious, since pressures substantially exceeding p_{min} may be needed to produce a melt. In the shock wave the material passes through all pressures from $p = 0$ to p_{min} and may be partially melted at any intermediate p , which corresponds to a latent heat of melting λ_p . Therefore, to produce complete melting at p_{min} it is necessary for the specific internal energy acquired on shock compression to be in the range between ϵ_1 and ϵ_2 :

$$\begin{aligned}\epsilon_2 &= \lambda_p + c(T_{min} - T_0) + \epsilon_x, \\ \epsilon_1 &= \lambda_0 + c(T_{min} - T_0) + \epsilon_x,\end{aligned}$$

where λ_p and λ_0 are the latent heats of fusion at $p = p_{min}$ and $p = 0$; T_{min} , minimal melting point under pressure; T_0 , initial temperature; and ϵ_x , energy of cold compression at $p = p_{min}$. It is assumed that the specific heat c is independent of temperature, while the latent heat of melting λ varies monotonically with pressure, and λ_p corresponds to the minimum value. If the relationship is not monotone, it is necessary to take λ_0 and λ_p as the maximum and minimum values in the given pressure range. If the substance has acquired the energy required for melting and the duration of the shock wave is greater than the melting time at the given pressure, there will be molten material behind the shock-wave front. The experiments of [9-12] give an esti-

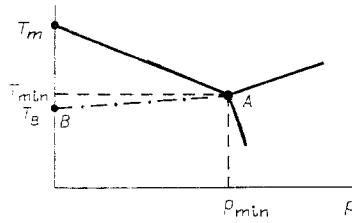


Fig. 1. Example of the phase diagram for a material with an anomalous pressure dependence for the melting-point curve.

TABLE 1

Material	T_m , K	T_{min} , K	p_{min} , kbar	$T_m - T_{min}$, K	Material	T_m , K	T_{min} , K	p_{min} , kbar	$T_m - T_{min}$, K
Ge	1210	723	95	487	InSb	798	593	25	205
Si	1688	1000	115	688	InAs	1173	773	100	400
Ce	1077	933	33	144	InP	1373	973	125	400
Ba	1002	773	65	229					

mate for the melting time of less than 10^{-6} sec. The melting can be accelerated if the material is preheated to a temperature close to T_m while retaining its crystalline structure.

We consider the scope for performing this process for Si, which has a high melting point, a high latent heat, and the maximum $T_m - T_{min}$ difference. For this purpose we elucidate how λ is dependent on pressure. One can estimate its change from Clapeyron's equation

$$\frac{dT_m}{dp} = \frac{T_m \Delta V}{\lambda},$$

where ΔV is the volume change on melting. The derivative of the melting point with respect to pressure is approximately constant up to 115 kbar [7]. Therefore,

$$\lambda_p \approx \lambda_0 \frac{T_{min}}{T_m} \frac{\Delta V}{\Delta V_0}.$$

Here ΔV and ΔV_0 are the volume changes on melting at T_{min} and T_m . The volume change on melting for a material with an anomalous behavior for the melting point is related mainly to the change in the mutual disposition of the atoms. Application of pressure makes the material more closely packed. One therefore assumes that $\Delta V \leq \Delta V_0$, and therefore

$$\lambda_p \leq \lambda_0 \frac{T_{min}}{T_m} \approx 0.6\lambda_0.$$

One can estimate ϵ_x from the shock adiabat for monolithic Si [13]: $\epsilon_x \approx 1/2 \cdot p \Delta V_a$, where ΔV_a is the change in specific volume on shock compression at $p = 115$ kbar, $\Delta V_a \approx 0.05 \text{ cm}^3/\text{g}$. As $\lambda_0 = 1.78 \cdot 10^{10} \text{ erg/g}$ [7] and $c = 0.89 \times 10^7 \text{ erg/g} \cdot \text{deg}$ [14], we get $\epsilon_1 = 2.72 \cdot 10^{10} \text{ erg/g}$ and $\epsilon_2 \leq 2 \cdot 10^{10} \text{ erg/g}$.

We now estimate ϵ for shock compression of porous Si whose initial density ρ_0 is half the density of monolithic Si. For the purpose of the estimate we assume that the density at the front alters by about a factor of two, and then we get for $p = 115$ kbar that

$$\epsilon = p/4\rho_0 \approx 2.4 \cdot 10^{10} \text{ erg/g}.$$

This value of ϵ is in the range between ϵ_2 and ϵ_1 . It is clear that heating the material ahead of the front to 350°C will cause ϵ to approach ϵ_1 . By increasing ρ_0 , one can reduce ϵ to ϵ_2 . Therefore, it is fairly easy for Si to realize the conditions for melting behind the shock-wave front. Similar calculations can be performed for other materials.

To obtain a homogeneous melt, it is necessary that all the internal energy ϵ acquired by shock compression is uniformly distributed over the volume. A sufficient condition for this is a small value for the thermal relaxation by comparison with the time of action of the pressure, which can be provided by a small value for the fraction. In shock compression of a powder, the temperature is unevenly distributed over the volume. However, at pressures of about 100 kbar, even the coarse fraction of a powder (about 0.5 mm) is in conditions

close to equilibrium at the shock-wave front (in times of about 10^{-7} sec) [15], because the particles at high pressure undergo considerable plastic strain, which results in more rapid thermal equilibration in the shock-compressed material for a comparatively coarse fraction by comparison with the characteristic time of thermal conduction. Also, shock compression of a porous specimen is characterized by very high heating rates (about 10^{10} °K/sec [15]), which is a distinctive feature of the process.

To demonstrate the reality of this process, we performed experiments with Si (specific resistance about $14 \Omega \cdot \text{cm}$) with an initial density approximately half of that for the monolithic material. The silicon particles before the experiment were of single-crystal type and had sizes of about 0.1 mm. After shock compression at a calculated pressure of 115 kbar, powder patterns were recorded with $\text{FeK}\alpha$ radiation. The (111) and (422) lines were recorded. We determined the fine-structure characteristics by x-ray diffraction – the size of the coherent-scattering regions D and the microstresses $\Delta a/a$ (where Δa is the deviation and a is the lattice parameter) [16] – which gave $D \approx 1.33 \cdot 10^{-5}$ cm and $\Delta a/a \approx 0.46 \cdot 10^{-3}$. A microcrystalline structure was obtained, which was evidently due to the formation of a supercooled melt and subsequent rapid crystallization.

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