The Heat Transfer Characteristics of PTFE During Quasiadiabatic Decompression in Nitrogen Gas

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Synopsis

This article describes a series of experiments which elucidate the origin of a previously reported apparent plasticization of PTFE under a high pressure N_2 environment. The results indicate that, to a first order, the apparent plasticization process is associated with the heat generated following a near adiabatic compression of the pressure environment; it is not a true isothermal plasticization in the conventional sense. The processes which contribute to this phenomenon involve subtle effects which are explored in some detail. Particularly important is the surprisingly high efficiency of the compressed gaseous media as heat transfer fluxes for intrinsically poor thermal conductors such as organic polymers. Other factors include the thermal conductivity of the gas and its heat capacity. In addition, the polymer itself manifests an intrinsic increase in its thermal conductivity due to the action of the triaxial stress. The overall temperature rise due to gas compression is very large and for N_2 long sustained. The work done on the polymer by simple triaxial compression is trivial in comparison; studies in liquid media confirm this to be the case. A less extensive treatment, along similar lines, is described for the decompression of gaseous media. The combined action of gas compression and decompression together with the associated thermal cycles are briefly discussed in the context of polymer processing and the behavior of PTFE compression seals.

INTRODUCTION

In 1971, Billinghurst and Tabor[1] reported an apparent plasticization of PTFE in an N_2 pressure environment. This effect was manifested as an initial small increase in shear modulus of short duration followed by a comparatively large decrease in modulus. The magnitude of this decrease increased with time and was more pronounced at higher initial temperatures and was found to decrease with increasing crystallinity (see Fig. 1). Changing the pressure medium to He or an hydraulic oil resulted in a linear increase in the shear modulus; no subsequent decrease was observed. The initial conclusion was that N_2 gas at high pressure plasticized the PTFE. It was these unusual results which, in part, stimulated a series of studies by the present authors.[2-4] In this article, we describe some experiments which are used to show that the apparent plasticization process is a consequence of the increase in temperature and the changes in the heat transfer properties of the polymer and the surrounding environment following a rapid increase in pressure. The experiments adopted to elucidate this process consist of monitoring the temperature rise in the polymer matrix and that of the surrounding environment following a relatively rapid pressure increase (typically from 0.1 MPa and room temper-
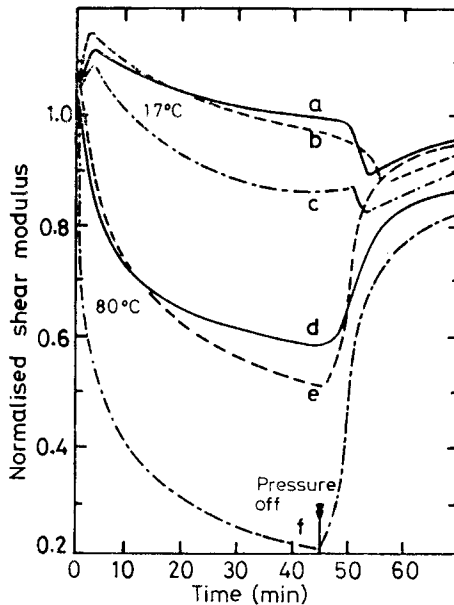
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Fig. 1.   PTFE plasticization curves under nitrogen pressure environment at 34.5 MPa pressure: (—) 68% crystallinity; (---) 65% crystallinity; (·····) 60% crystallinity.

ature to 34.5 MPa in 15 s). The corresponding temperature responses following a rapid depressurization to atmospheric pressure are also reported. The results of experiments in which the polymer specimen is in equilibrium with an N_2 pressure environment and is externally and isobarically heated at a controlled rate are also described. A marked increase in the thermal conductivity of the polymer is observed when it is under pressure.

Publications[2-4] by the present authors using similar PTFE samples and pressure media have reported data on the mass sorption of gas in the polymer, and associated volumetric changes at thermal equilibrium. The current study while prompted by the interest in apparent plasticization was mainly undertaken to define the conditions, particularly the time, required to achieve thermal equilibrium in polymer specimens subjected to high gas pressures. The equilibrium results have several implications in the evaluation of the current transient or nonequilibrium studies. The main ones are related to the extent of the mass sorption and the volumetric changes measured in the polymer. The mass sorption of gas is a function of the gas, the pressure, and the temperature. In the current range of variables discussed here the mass sorption is a linear function of the ambient gas density almost irrespective of the gas. The temperature dependence of the equilibrium mass sorption does, however, depend upon the gas; for helium it is small but for nitrogen it is comparatively large. The main point, however, is that significant quantities of gas are sorbed typically 15% by volume if it is assumed that the internal gas density is the same as the ambient density. The volume sorption calculated in this way is the greater for small molecules under similar ambient conditions. The equilibrium volume change in the polymer depends upon many factors but to a first order the volume change observed in gas media is comparable with that observed in hydraulic fluids.
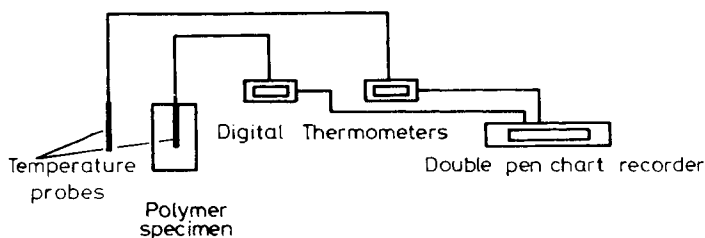
Fig. 2. Schematic arrangement of the differential thermal analysis (DTA) apparatus used to monitor the temperature change in the polymer and the surrounding pressure medium.

EXPERIMENTAL

The basic arrangement of the differential thermal analysis experiment is schematically represented in Figure 2. The temperatures of the polymer and the pressure media are measured by monitoring the changes in the resistance of platinum film thermometers (type 158–328; Radio Spares, $\pm 0.1°C$ accuracy) placed inside and on the surface of the PTFE specimen. In the former case, the platinum film (ca. $30 \times 4 \times 0.5$ mm) is encapsulated by a cylindrical (ca. 42×17 mm) block of PTFE specimen. This is achieved by firmly inserting the platinum film into a notch machined inside the smaller cylindrical block (ca. 30×8 mm) which is machined out of the original polymer. Finally, the unit is assembled by inserting the notched block containing the platinum film inside the original polymer and firmly sealing the top end using another suitably machined PTFE block. The various PTFE components before assembly are shown in Figure 3. The temperature of the pressure medium is measured by simply fastening a platinum film onto the surface of the PTFE specimen using PTFE tape. Various attempts to mold the platinum film thermometer inside the PTFE specimen failed due to the breakage of the film during the polymer preforming process. The use of thermocouples as temperature probes was also unsuccessful due to complications associated with the creation of spurious potentials at the additional junctions formed between the thermocouple wire (copper) and the electrical connections (invar)
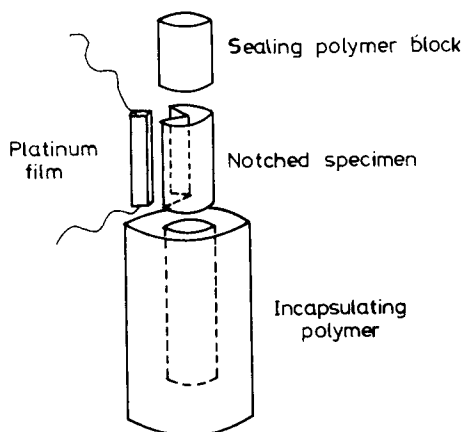

Fig. 3. Schematic layout of the various components of a PTFE block used for the DTA experiments.

in the pressure vessel cap. The variation of temperature of the two probes with time was recorded using an ultraviolet recorder (NEP; type 2500). The thermal lag and local perturbations produced by the current probes is discussed later. The pressure vessel employed had an I.D. of 5.12 cm with an aspect ratio of 2.5. Pressurization was achieved using a Charles Madan gas booster pump. A more detailed description of the apparatus is published elsewhere.[3]

RESULTS AND DISCUSSION

Figure 4 shows the results of the kinetic heat transfer experiments carried out on a medium crystallinity PTFE specimen (2157 kg/m^3; 70% crystallinity) following its exposure to a pressure ramp in various pressure transfer media. Curves A, B, and C are, respectively, the temperature vs. time for He, N$_2$, and hydraulic oil following their adiabatic compression from 0.1 MPa and 17°C to a final pressure of 34.5 MPa in 15 s. Curves a, b, and c represent the temperatures generated by Billinghurst and Tabor[1] when studying the apparent N$_2$ plasticization of PTFE. The important features of the above results may be summarized as follows:
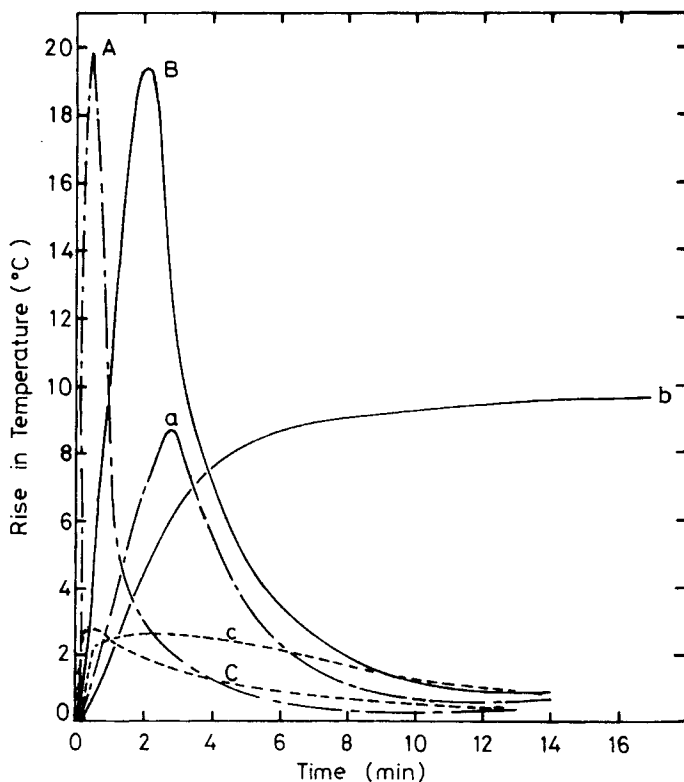

Fig. 4. The rise in temperature of PTFE and various pressure environments against time following a rapid pressurization from 0.1 to 34.5 MPa in 15 s. Curves A, B, and C are the response of He, N$_2$, and hydraulic oil pressure media, respectively. Curves a, b, and c, respectively, represent the corresponding PTFE response in the above pressure environments.

a. The temperature detected in the pressure media is primarily attributable to the thermal energy released following the adiabatic compression process. The gases being more compressible than liquids evolve a larger amount of heat.[5] The expected temperature rise associated with an *adiabatic* compression of a fixed number of moles of N_2 exposed to the above conditions is ca. 1200°C (see later).

b. The detected rate of rise in the temperature of the pressure media is limited by the rate of change in the resistance of the platinum probe in response to a rapid change in ambient temperature. The faster response in He (curve A) compared to N_2 (curve B) is partly due to the larger thermal conductivity of helium (ca. 5 folds greater than N_2 at 40°C and 34.5 MPa)[6] together with a more efficient heat transfer by forced convection[7] as a consequence of the larger atomic velocity and hence the smaller viscosity of He atoms.[8]

c. The corresponding rise measured in the temperature of the polymer may be partly attributed to the triaxial compression of the polymer[9,10] as well as the increase in the ambient temperature. In the former case, it is readily shown that,[11] for a reversible adiabatic compression, the rise in temperature of the polymer with increasing pressure is given by

$$\left(\frac{\partial T}{\partial P} \right) = \left(\frac{\alpha V T}{C_p} \right)$$

where α, V, and C_p are the coefficient of volumetric expansion, specific volume, and specific heat capacity at constant pressure respectively. In the case of PTFE at $T = 17°C$,[12] $\alpha = 6 \times 10^{-4}$ K^{-1}, $V = 4.636 \times 10^{-4}$ m^3 kg^{-1}, and $C_p = 1.247$ kJ (kg K)$^{-1}$; $(\partial T/\partial P) = 6.7 \times 10^{-2}$ °C/MPa. The corresponding estimated temperature rise due to a triaxial compression of PTFE up to 34.5 MPa from 17°C and atmospheric pressure is therefore ca. 2.3°C. Interestingly, this value is in close agreement with the value obtained in the hydraulic oil medium (curve c).

Bearing in mind that the magnitude of the equilibrium volumetric strain produced in gaseous media is similar to that produced in hydraulic oils, it is therefore reasonable to assume that temperature rises due to the volumetric change in the polymer are similar in the two cases.

The inevitable increase in the thermal conductivity of the polymer as a result of a reduction in its free volume, following the application of pressure[13-15] especially around room temperature,[16,17] is another influential factor affecting the temperature change detected in the polymer. Figure 5 is the measured response of a PTFE specimen heated at atmospheric pressure in air (curve A) or isobarically heated in a high pressure (34.5 MPa) N_2 medium (curve B). The marked improvement in the efficiency of heat transfer in the high pressure environment is clearly evident. Apart from the intrinsic improvement in the thermal conductivity, another important process governing the efficiency of heat transfer is the reversible absorption of the hot gas flux in the polymer matrix.[2,18,19] It may be useful to bear in mind that the smaller He atoms diffuse faster than the larger N_2 molecules,[2] and both are sorbed quite strongly. This is consistent with the observed smaller rate of increase in the
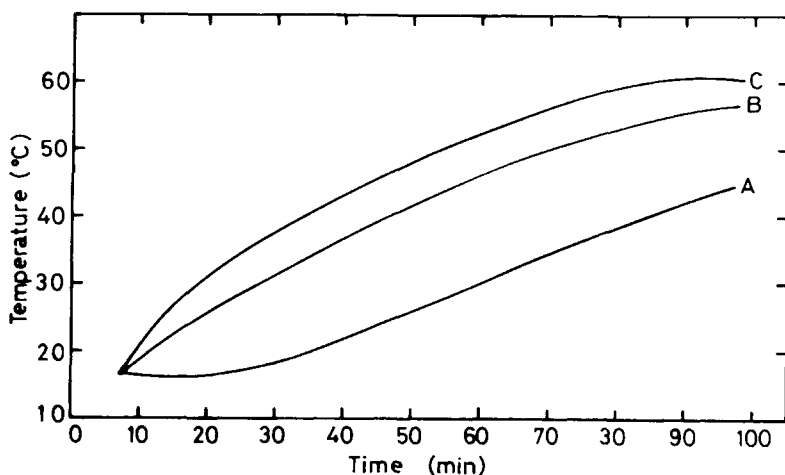
Fig. 5. The rise in temperature of PTFE against time in air at atmospheric pressure (curve A) and in N_2 at 34.5 MPa (curve B) when both are heated at a controlled heating rate represented by curve C.

temperature of the polymer in the N_2 pressure medium, although it may not be the complete explanation.

The transfer of heat energy from the pressure media to the polymer matrix via simple interface thermal conduction is also significant. The final temperature is limited by the total work, the heat capacity, and the rate of heat loss during the thermal equilibriation of the polymer and the pressure media with the pressure chamber (at 17°C) at the end of the compression cycle. This is proportional to the thermal conductivity K of each medium. The values of K for He, N_2, and an hydraulic oil at 34.5 MPa and 40°C are 0.172, 0.043,[6] and 0.09 W/m °C,[20] respectively (the variation of K with temperature is assumed to be small). The above is reflected in the rapid thermal equilibriation of the polymer in He pressure medium (curve a).

At this stage the data of Billinghurst and Tabor cited earlier can be explained in general terms. It is evident from Figure 4 that the polymer specimen in an N_2 pressure medium reaches a temperature of 26°C (9°C higher than the starting temperature) some 18 min after the completion of the chosen compression cycle. Billinghurst[21] himself established a large temperature dependence for the shear modulus of PTFE at atmospheric pressure and around the room temperature transition.[22] These data are reproduced in Figure 6. It is evident that in the generation of a 10°C rise in the temperature of the PTFE from 17 to 27°C (a condition similar to that produced by Billinghurst) will produce a 40% drop in modulus. Also the larger temperature dependence of the shear modulus for the more highly crystalline polymer is consistent with the reported larger effective plasticization of the polymer with increasing crystallinity (see Fig. 1).

The increase in the effective plasticization with the initial temperature may be rationalized as follows. Considering an adiabatic compression of a fixed number of moles of N_2 from a temperature T_1 and pressure P_1 to a final pressure P_2, the rise in temperature, ΔT, assuming ideal gas, is given by[5]
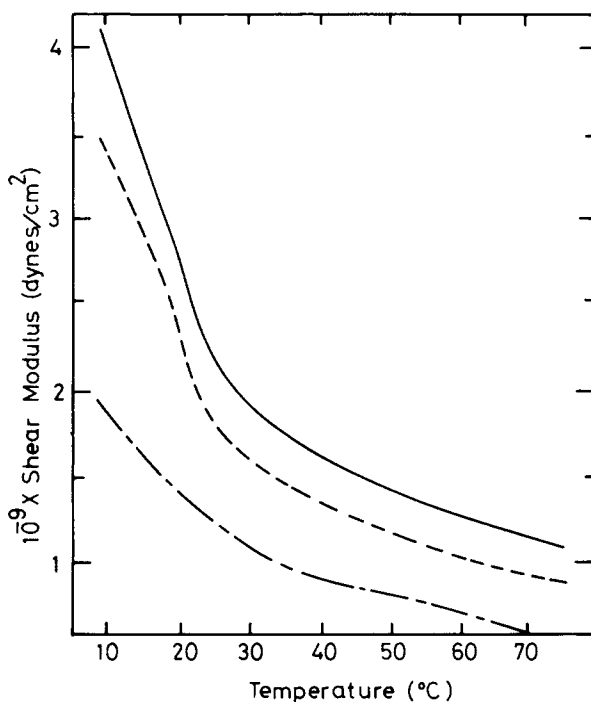
$$\Delta T = T_1\left[(P_2/P_1)^{0.286} - 1\right]$$

Fig. 6. The variation of the shear modulus of PTFE with temperature at atmospheric pressure: (—) 68% crystallinity; (---) 65% crystallinity; (-·····-) 60% crystallinity.[21]

For an initial temperature $T_1 = 17°C$ and a pressure ratio $P_2/P_1 = 340$ (curves a, b, and c; Fig. 1), the rise in temperature $\Delta T = 1246°C$. Alternatively, for the same conditions but with $T_1 = 80°C$ (curves d, e, and f; Fig. 1), $\Delta T = 1500°C$. The above argument indicates that the rise in the temperature of gaseous media and hence the temperature rise in the polymer directly increases with the initial temperature of the pressure medium before the compression cycle. This is again consistent with the observed increase in the effective plasticization of PTFE with the initial ambient temperature. The *detected* rise in the temperature of the pressure medium is, however, very much lower than the predicted values. This may be attributed to the loss of a significant proportion of the heat generated through the pressure vessel walls, the finite heat capacity of the temperature probe, and an increase in the number of moles of gas at the end of the compression process (in this case, pressurization is achieved by increasing the number of moles of gas in a fixed volume). Further the heat transfer characteristics of the gas to the solid is relatively inefficient. Calculation of the observed temperature rise ΔT for the above system has proved to be intractable. However, similar trends may be expected.

Billinghurst and Tabor were not able to detect these temperature rises in part due to the very slow response of the thermocouple temperature probes (ca. 2 mm diam copper wire) employed in their work. As an example, the thermal equilibrium time for a 0.8 mm diam copper wire originally at 150°C and suddenly exposed to air at 40°C is more than 30 min.[7] The corresponding equilibrium time for a 2 mm diam wire is considerably longer.
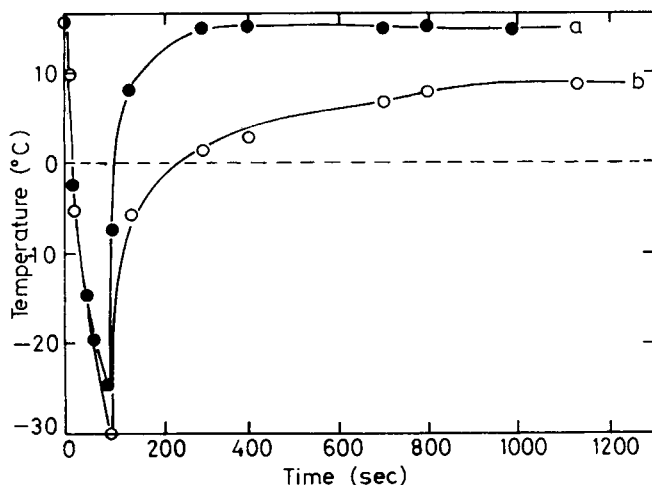
Fig. 7.   The temperature response of the PTFE (●) and the surrounding ambient (○) following a rapid depressurization from an N_2 pressure of 34.5 MPa and room temperature to atmospheric pressure in 15 s.

Finally, Figure 7 shows the response of a PTFE specimen (curve a) following a rapid decompression from an N_2 pressure of 34.5 MPa and room temperature to atmospheric pressure. The corresponding temperature probe response of the ambient is also presented in the same figure (curve b). The rapid decompression results in a marked (ca. 50°C) drop in the measured temperature of the polymer. In some cases, the above is accompanied by the formation of small blisters on the surface of the polymer. Normally it is only possible to examine the polymer no sooner than ca. 30 min after decompression. During this period we presume that many of the original blisters have collapsed and only a fraction remain. Significant amounts of gas are sorbed within the polymer under pressure.[4] When the pressure is reduced rapidly the gas solubility significantly decreases.[4] This gas then may nucleate to form internal bubbles which will expand as the hydrostatic stress is reduced and then rupture, or serious deformation in the polymer ensues. During this process, the large reduction in the temperature of both the polymer and the ambient is critical and is sufficient to produce a substantial reduction in the equilibrium mass gas sorption and the rate of gas desorption from the polymer. In addition, the polymer becomes stronger (increase in modulus) which increases the stored stresses associated with the growing bubbles. Finally, the toughness of the matrix is reduced as is its ability to creep to accommodate the internal stress. A full account of these processes is described elsewhere.[23]

These features have certain implications in the optimization for the conditions required for hydrostatic gas annealing of PTFE and the polymer's use as seals in gaseous environments where rapid pressure fluctuations occur. Significant and permanent increases in density for PTFE can be achieved by the routes described above, typically 3%. The transient hot gas flux provides very effective heat transfer combined with an hydrostatic stress; the volume contraction in gases is comparable to that detected in liquids.[3] Providing the gas is desorbed properly, this enhancement of density can be preserved by the natural and rather uniform thermal quenching generated during decompres-

sion. The indifferent behavior of PTFE seals in certain gaseous environments, while not precisely correllatable at present with these gas environment/polymer interactions, is probably partially caused by the processes described.

CONCLUSION

In this article, the origin of a previously reported apparent high pressure N_2 plasticization of PTFE was investigated in some detail. The experimental data are consistent with the view that the apparent plasticization process is a consequence of the temperature rise associated with an almost adiabatic compression process of the N_2 pressure medium and to a much lesser extent that of the polymer matrix. The magnitude and the duration of the plasticization was found to depend, to a first order, on the thermal energy released during the compression cycle and on the rate of heat loss from the polymer to the surrounding medium, respectively. There are important secondary factors such as the degree of crystallinity of the polymer and the degree of sorption and rate of diffusion of the gas pressure medium in the polymer matrix.

In spite of the current conclusion that the apparent plasticization process is largely thermally induced by rather unusual processes and is thus not of the conventional sort, it does appear that gaseous media can provide a detectable "real" plasticization of PTFE. The effect is, however, not restricted to nitrogen. Some gaseous media, for example, produce a pressure dependence of the 20°C transition in PTFE which is measurably less than that obtained with hydraulic fluid media. In this sense the gas may be regarded as a true, even if modest, plasticizer for PTFE. These data are described elsewhere.[24,25]

From a practical point of view, the above result has some important implications. The conveying of many hydrocarbon gases, in the process industry for example, involve high pressure reciprocating pumps incorporating self-lubricating PTFE seals. In many cases, the rapid and very marked change in the temperature of the polymer as a result of the pulsating action of these pumps following compression and depressurization results in a catastrophic failure of these seals. It is known that the performance of these seals is often very sensitive to the environment particularly the gas.[26] Many systems fail unexpectedly and the failure seems to be thermally induced. Clearly the gas medium can influence the surface temperature in a subtle way, and it is interesting to speculate that the sorption/desorption process described above is an influential factor.

On a different topic, the final step in the manufacture of PTFE involves the sintering followed by cooling[27] of the compacted polymer at a controlled rate. Rapid cooling or heating results in a nonhomogeneous and sometimes highly defective end product. The advantages in using a superimposed high pressure helium environment during the finishing process are clear and potentially attractive.

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