

Figure 3 Scanning electron micrograph of the fracture after heat-treatment G to form nearly 50 vol % Ti_2Ni_3 .

the inherently brittle phase or the obstruction of slip in the β -phase. While the mechanical behaviour of the Ti_2Ni_3 phase is unknown, it is reasonable to expect that plastic deformation of Ti_2Ni_3 occurs with difficulty. Since failure in β -TiNi is largely of a ductile nature, the operative mechanism is then most likely associated with crack propagation in the grain boundaries and the barrier to slip imposed by the Ti_2Ni_3 phase. In discussing the second phase barrier to slip, Silcock [5] has shown that if three of the $\langle 111 \rangle$ slip directions in a given bcc matrix are not parallel with the likely slip-directions in a given second phase, then rupture of strong bonds are required for the remaining slip-direction. Ashby [6] has shown that the resultant increase in work hardening associated with the interaction of primary glide-dislocations with the forest-dislocations created about the second phase can be expressed as:

$$\tau - \tau_0 = KG_m \left[\frac{bV\gamma\rho}{d} \right]^{1/2}$$

where G_m is the shear modulus of the matrix, V is the volume fraction of the second phase, $\gamma\rho$ is the plastic shear strain on the primary slip-system, and d is an effective diameter of the second phase particles. The constant K has been

found experimentally to be near 0.2. By equating the shear stress difference $\tau - \tau_0$ to the difference in tensile stress between fracture and yielding of polycrystalline β -TiNi, $(\sigma - \sigma_0)/m$ where m is 2.7 for bcc metals) then the plastic shear strain required on the primary system is in the vicinity of macroscopic yielding (10^{-2} to 10^{-3}). Thus, the apparent brittle behaviour of ϵ -containing alloys is related both to the hard Ti_2Ni_3 phase which increases the rate of work hardening of the β -phase and to crack propagation along brittle grain boundaries. Failure occurs by crack propagation in the grain boundaries and some type of "interphase" fracture which is quasi-ductile on a microscopic scale. It is important to note that 85% of the fractured surfaces were intergranular and 15% were transgranular.

The attainment of high strengths in Ti-55Ni at room temperature with the retention of some ductility should be possible by controlling the volume fraction of ϵ by appropriate heat-treatment, or through alloying. In general, good tensile properties may be obtained if $TiNi_3$ can be dispersed throughout the β -matrix. The value of the duplex heat-treatment is to produce a fine dispersion of $TiNi_3$ which subsequently transforms to Ti_2Ni_3 . Thus, it is possible to attain attractive tensile properties through such duplex heat-treatment.

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Direct measurements of the reverse stress asymmetry in the yielding of anisotropic polypropylene

In our previous work we have recognized an asymmetry between the tensile and compressive

yield behaviour of oriented polymers [1]. Most of our previous measurements have been made either in tension or simple shear on drawn polymer sheets and similar results have been obtained by other workers [2-4]. The measurements provide only an indirect measure of the

asymmetry. Direct measurements have been performed on cold drawn injection moulded polyethylene terephthalate (PET) [5], and on cylinders wound from sheets of drawn PET [6] but the absolute magnitudes of compressive yield stresses were imprecise due to the poor specimen design which was dictated by material availability.

We now wish to report what we believe to be the first reliable measurements of tensile and compressive yield strengths of a series of hydrostatically extruded polypropylene. The material was kindly supplied by Imperial Chemical Industries Ltd, Petrochemical and Polymer Laboratory, Runcorn, to whom we are indebted.

Measurements of birefringence and wide angle X-ray diffraction pictures indicated that over the range of extrusion ratios reported here, the extrusion process produced a comparable degree of orientation to that produced by cold drawing this polymer, e.g. the birefringence of the 5:1 extrudate was found to be 2.34×10^{-2} .

All experiments were conducted using a conventional Instron machine. Compression measurements were made using a compression cage to produce a compressive load on the specimen with the machine in its tensile mode. The cage was equipped with linear displacement

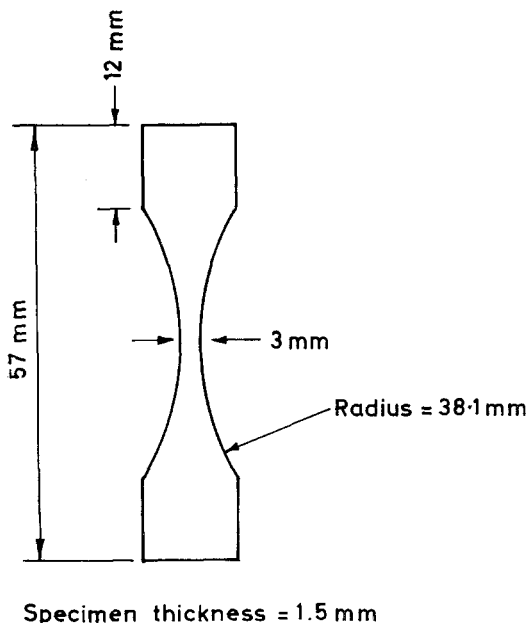


Figure 1 Tensile specimen design.
 *1kb $\equiv 10^9$ dyn/cm² $\equiv 100$ MN/m².

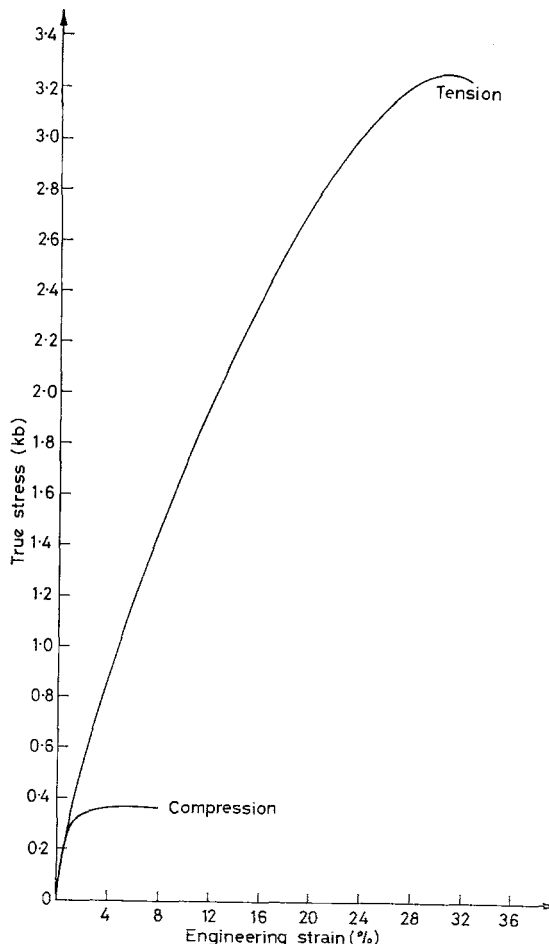


Figure 2 Typical stress-strain curves in tension and compression. Extrusion ratio = 5.0.

transducers to monitor accurately strain in the specimen. The compression specimens were machined from the extruded rod to produce cylinders 6 mm diameter, and 5 mm in length.

The tensile specimens were machined to form waisted strips with dimensions as shown in Fig. 1. Tensile strains were obtained from the Instron chart, compensating for machine deflection, and the effective gauge length of the specimen calculated assuming ideal elasticity. Both tensile and compression specimens were cut with their axes parallel to the extrusion direction. True stresses were calculated using the measured axial strain assuming constancy of volume.

Typical true stress-strain curves for both tension and compression are shown in Fig. 2.* The tests were made at room temperature and at a strain rate of 1.667×10^{-3} sec⁻¹. The exact

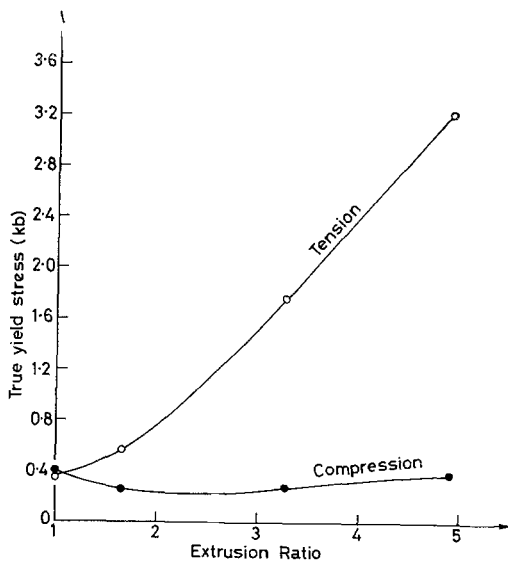


Figure 3 Variation of tensile and compression yield stresses with extrusion ratio $T = 22^\circ\text{C}$ $\dot{\epsilon} = 1.7 \times 10^{-3}/\text{sec}$.

point on the stress-strain curve which marks the onset of irrecoverable deformation depends in a complicated manner on many variables, and so here we take the first maximum as a measure of the yield stress.

Fig. 3 is a plot of the yield stresses in tension and compression as extrusion ratio. The curves show two distinct regimes.

1. At very low extrusion ratios the compressive strength is greater than the tensile strength. This result is consistent with the reported effect of the hydrostatic component of stress on the yield behaviour of polymers [7] and can be simply

interpreted as due to the change in the sign of the hydrostatic component between the tensile and compression tests.

2. At higher extrusion ratios the influence of hydrostatic pressure is overwhelmed by the effects of orientation. The results can be understood in terms of the relative ease of compressing an oriented structure of extended chains compared with extending it further, as we have discussed elsewhere [1].

Further measurements are now being made over a wide range of temperatures and strain-rates to provide data for a more comprehensive understanding of these effects.

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The nitriding of silicon powder compacts

A versatile route for the production of silicon nitride ceramic is reaction-sintering. Silicon powder (particle size usually $< 75 \mu\text{m}$) is first formed into a compact by any one of a number of techniques, but frequently by isostatic pressing in the pressure range 50 to 200 MNm^{-2} . The shaped compact is then heated in the temperature range 1250 to 1450°C in a nitrogenous atmosphere when the silicon nitride ceramic is formed. Depending upon the size of the compact being nitrided, sintering times above 120 h can be encountered [1].

It is our object to understand the nitriding mechanism and in particular to identify the

reaction rate-controlling process and our starting point is the recognition that the overall nitriding of a compact occurs by the following two steps: (i) the diffusion of the nitrogen-bearing gas into the compact, (ii) the reaction of the nitrogen with individual silicon particles.

Each one of these steps is complex in itself and the second is the subject of another note to be published in this Journal; it is with the gaseous diffusion that we are concerned here.

That gaseous diffusion could be the rate-determining step for compacts above a certain size is self evident and this is intuitively allowed for by the manufacturer. However, a quantitative understanding of this aspect is difficult to achieve because the microstructure of the nitrid-