Rhines [6] has been criticised on experimental grounds [7]. Furthermore, the work by Spear and Gardner [8] originating the dendrite spacing/cooling-rate correlation the authors advocate, *itself* contains unambiguous evidence of a marked effect of alloy constitution. When expressed as a power relation, in line with other measurements [1], the effect of composition, they [8] find, for example, is at least as great as that of cooling-rate. The authors' unqualified statement that "Hence the dendrite arm spacing method can safely be applied to all alloy systems" seems precipitate in relation both to this evidence and to all that is available, amounting to measurements on just a few (mainly Al-base) systems over restricted ranges of variables.

On the fifth point, the Nusselt number of 0.03 for the grit-blasted substrate indicates that cooling is only just within the lower bound [9] of the intermediate cooling-range. Ruhl's calculations [9] show [10] that the assumption of Newtonian conditions under such circumstances* introduces an error of considerably less than a factor of two which is certainly not greater than other sources of error and uncertainty in this and in other methods.

The attraction of the dendrite method is undoubtedly its ease of application and wide opportunity for use. This is no reason for disregarding the limitations of its present basis and for advocating its universal use without qualification. Obviously, spot checks by alternative methods are a minimal safeguard and there is clearly a general need to check one method against another on common systems. This is the approach which will enable present *estimates* to be improved, and, ultimately, to be superseded by *measurements*.

References

1. M. H. BURDEN and H. JONES, *J. Inst. Metals* **98** (1970) 249.
2. H. MATYJA, B. C. GIESSEN, and N. J. GRANT, *ibid* **96** (1968) 30.
3. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
4. P. PREDECKI, A. W. MULLENDORE, and N. J. GRANT, *Trans. Met. Soc. AIME* **233** (1965) 1581.
5. B. C. GIESSEN and R. H. WILLENS, in "Phase Diagrams: Materials Science and Technology", vol. 3, Ed. A. M. Alper (Plenum Press, New York, 1970), p. 103.
6. B. H. ALEXANDER and F. N. RHINES, *Trans. AIME* **188** (1950) 1267.
7. J. A. HORWATH and L. F. MONDOLFO, *Acta Metallurgica* **10** (1962) 1037.
8. W. E. BROWER, R. STRACHAN, and M. C. FLEMINGS, *Cast Metals Res. J.* **6** (1970) 176.
9. R. C. RUHL, *Mater. Sci. Eng.* **1** (1967) 313.
10. H. JONES, *ibid* **5** (1970) 297.
11. R. E. SPEAR and G. R. GARDNER, *Trans. Amer. Foundrymen's Soc.* **7** (1963) 209; (*Modern Castings* **43** (5)).

Received 1 December
and accepted 8 December 1971

H. JONES
Department of Metallurgy
University of Sheffield, UK

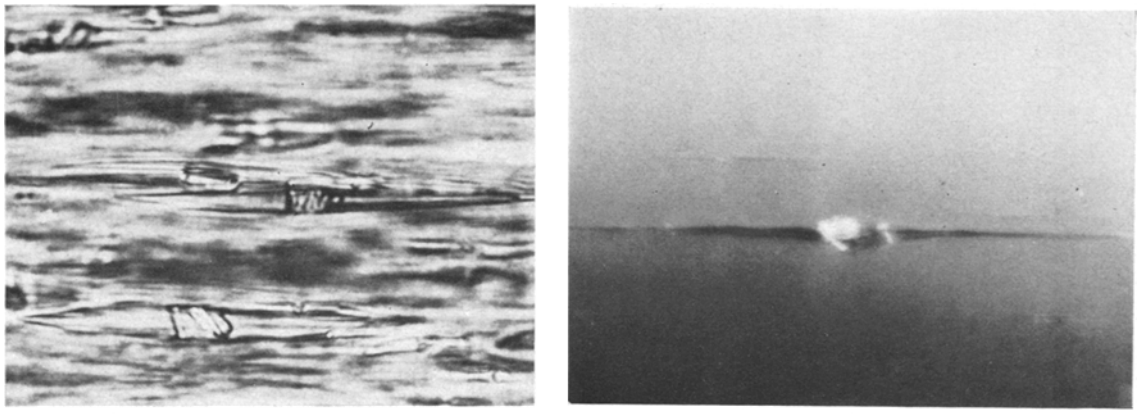
*Brower *et al* [8] reached the same conclusion for an even higher Nusselt number (0.5) observed in splat-cooling

*Observations during Annealing of Cold-Drawn Polyethylene**

This letter describes some preliminary observations made during cold drawing and subsequent annealing of bulk-crystallised linear polyethylene. The structures that are observed to develop during annealing on a microscope heating stage are probably due to the presence of low molecular weight fractions.

Sheet specimens, 0.2 mm thick, of compression moulded Rigidex 2 high-density polyethylene were observed during cold drawing by a micro-tensile machine fitted to a Zeiss photomicroscope. The polyethylene contained particles of silica catalyst, ranging up to 25 μm diameter, which initiated the formation of cavities during the cold-drawing process. The natural draw ratio of 8 resulted in considerable elongation of the cavities, and the influence of the transverse tensions associated with the cold-drawn neck boundary are evident from the fact that the voids were very much wider in the plane of the sheet than perpendicular to it. Fig. 1a shows the outline of a void in as-drawn material and 1b a view of another void in a section perpendicular to

*This work was carried out at the University of Surrey, Guildford.



(a) (b)

Figure 1 (a) Voids in as-drawn polyethylene, viewed through the plane of the sheet (× 620). (b) Voids in as-drawn polyethylene, viewed through the edge of the sheet (× 435).

the sheet plane.

Certain specimens were annealed for a few minutes at a temperature of 130°C, close to the melting point of the material, and it was subsequently found that the previous smooth outline of the cavities had developed marked serrations, as shown in fig. 2. This unexpected phenomenon was investigated by observing the changes which occurred during the annealing cycle on a heating stage fitted to a Zeiss photomicroscope. Figs. 3a, b and c are taken from a time series of photomicrographs of a single void during heating and cooling. Fig. 3a shows the initial outline of the void, which is serrated due to a previous anneal. Fig. 3b shows the cavity when the specimen had attained its maximum temperature of 120°C, and it can be seen that the volume has apparently decreased considerably, particularly the lower part.

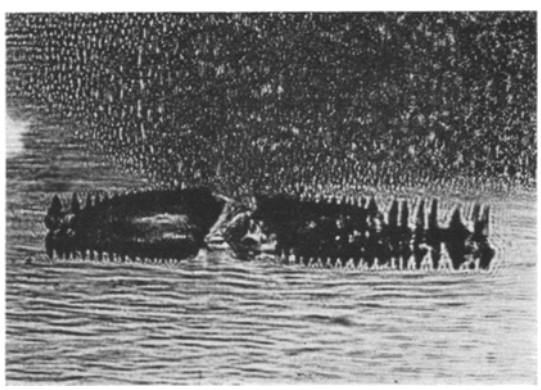


Figure 2 Serrated outline of a void in drawn and annealed polyethylene. A silica catalyst particle is situated at the centre of the cavity (× 400).

On cooling from 120°C little change was observed until the temperature had dropped to 108°C, when serrations began to form in the region between the old and new boundaries of the void. The serrated structure continued to develop during cooling from 108 to 90°C, below which no further change in outline could be detected (fig. 3c).

Later experiments using both the hot stage and an oil bath emphasised the importance of cooling rate in developing the serrated structure: low cooling rates appeared to inhibit its formation, while the highest rates attainable by quenching into liquid nitrogen developed pronounced serrations at almost all voids.

Observations relevant to the void annealing were also made at the free surface of the sheet specimens. During heating on the hot stage, the specimen buckled slightly and pressed against the cover glass, the presence of a thin fluid layer on the surface then became evident. Due to the curvature of the specimen surface, a number of meniscus boundaries were formed between the window and the specimen, and on cooling from the upper anneal temperature solidification occurred at these boundaries by pronounced acicular growth, as shown in fig. 4. Like the growth of serrations in the voids, the needles of solid were perpendicular to the draw direction, and grew in a series of discrete jumps from the

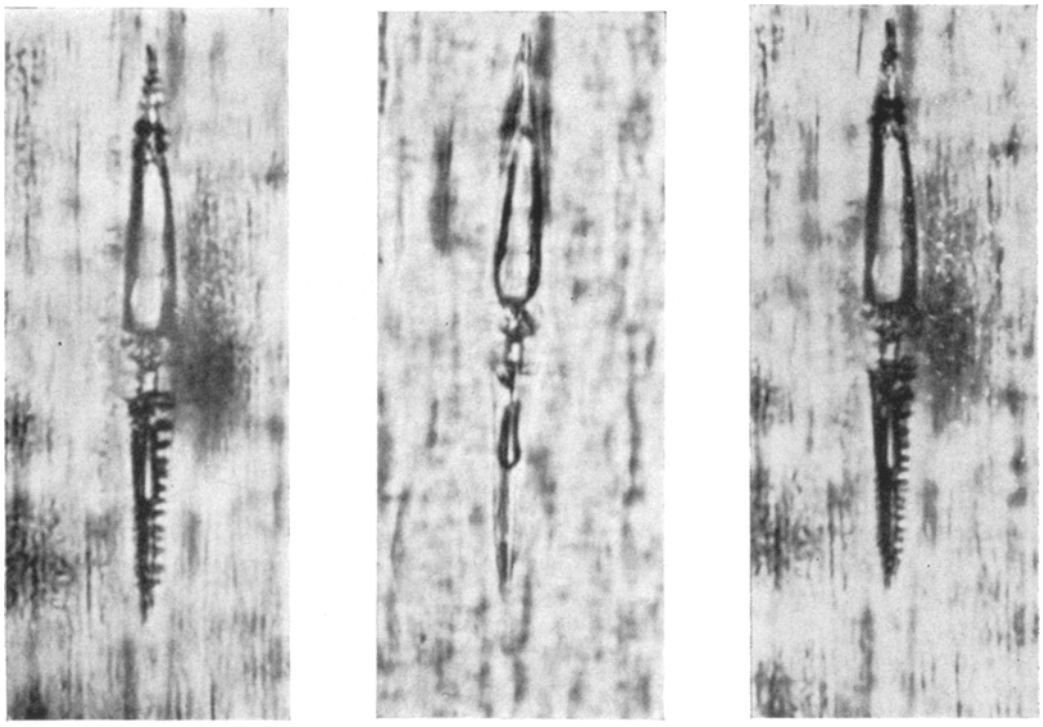


Figure 3 Time series of photographs of a void during heating and cooling (× 750). (a) Showing the initial state of the void in drawn and annealed material before reheating. (b) Showing the void of decreased size at 120°C. (c) Showing the void cooled to 90°C with the serrations reformed.

thicker to the thinner part of the fluid surface layer.

The temperature range of this acicular growth was from 115 to 110°C, but slower growth of more widely spaced needles was observed in the specimen temperature range 60 to 40°C. These were also perpendicular to the draw direction (fig. 5).

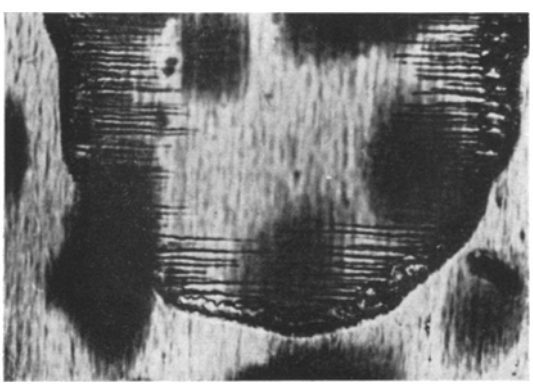


Figure 4 Acicular growth perpendicular to the draw direction, at the boundary of the wetted surface between the polyethylene and the cover glass (× 310).

A second phenomenon was found in the temperature range 115 to 110°C: the formation of a number of opaque regions about 200 μm in diameter, which proved on closer microscopic inspection to have a lamellar structure with a spacing of about 1 μm, as shown in fig. 6. These lamellae, though slightly irregular, had a general orientation perpendicular to the draw direction. On reheating, the structure disappeared in roughly the same temperature range as that in which it was formed. This structure was not restricted to the surface, but was found within the specimen as well. The Lamellar regions were not detected in the rapidly quenched specimens, in which pronounced serrations were found.

There are numerous points of interest in these

results. The formation of holes at foreign particles, and their subsequent growth during plastic deformation, is strikingly similar to the processes which initiate ductile fracture in metals [1]. Although the particle density of silica in the Rigidex 2 material is less than that of inclusions in metals, such particles may have an important influence on strength and fracture properties. In this note, however, we wish to consider the growth phenomena associated with cooling from temperatures of 120 to 130°C.

Most of the specimens described here had been annealed at some time just below the melting point of the bulk material. Thus the crystalline polyethylene lamellae are ordered so that, in the plane of the sheet, the long axis of each lamella is perpendicular to the drawing direction. The low temperatures at which the void "shrinkage" shown in fig. 3 occurred, and at which there was a

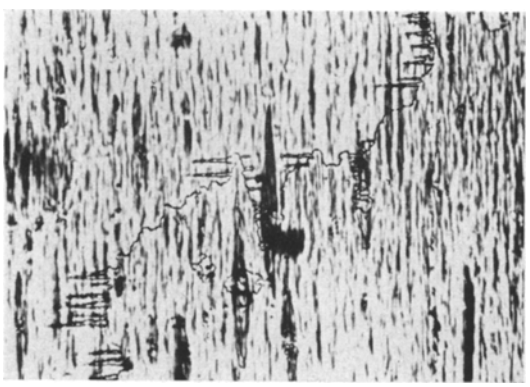


Figure 5 Low temperature acicular growth at the boundary of the wetted surface between the polyethylene and the cover glass (× 265).

fluid layer on the free surface, strongly suggest that both are due to the segregation of material of low molecular weight, low melting point polymer, as described by Geil [2]. Anderson [3] has reported that fractionation on the basis of molecular weight does occur, leading to separate crystallisation of the different molecular weight fractions. Calculations using the empirical equation of Broadhurst [4] would suggest that in the present case paraffin chains containing as few as 22 carbon atoms may be responsible for the crystallisation at temperatures as low as 40°C. Observations on the annealing of oriented high density polyethylene by Anderson [5] have shown that low molecular weight molecules exude to the

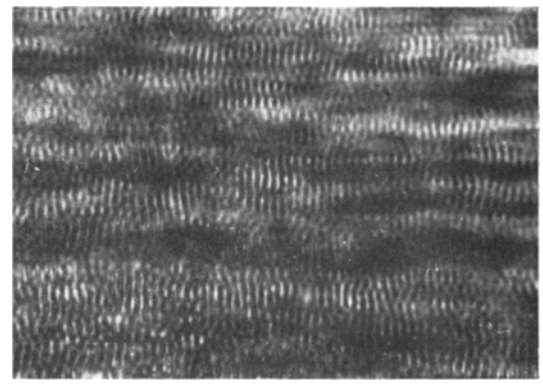


Figure 6 Lamellar structure formed within the polyethylene sample (× 1370).

sample surface, migrate and recrystallise epitaxially on this surface. The molecules recrystallised in the form of needle-like lamellae, arranged with their long axes perpendicular to the orientation axis of the sample. However, the scale of this growth was about an order of magnitude smaller than that seen in the present observations.

The lamellar structure of fig. 6, which occurs within the bulk of the specimens, forms and disperses in the same temperature ranges as the surface structures. It thus appears that this, too, is the result of solidification of low melting point material.

Acknowledgements

The authors wish to acknowledge the Science Research Council for financial support and Professor A. Keller for valuable discussions.

References

1. K. E. PUTTICK, *Phil. Mag.* **4** (1959) 964.
2. P. H. GEIL, Polymer Single Crystals, Polymer Reviews Vol. 5 (Interscience 1963).
3. F. R. ANDERSON, *J. Appl. Phys.* **35** (1964) 64.

4. M. G. BROADHURST, *J. Chem. Phys.* **36** (1962) 2578.
5. F. R. ANDERSON, *J. Polymer Sci.* **C8** (1965) 275.

Received 12 August
and accepted 2 November 1971

R. B. E. SMITH
BP Research Laboratories
Sunbury on Thames
Surrey, UK

L. E. MILLER
Department of Materials Technology
University of Technology
Loughborough, Leicestershire, UK

K. E. PUTTICK
Department of Physics
University of Surrey
Guildford, Surrey, UK

A Method for Laboratory Scale Melting and Solidification Studies of Cast Irons

Most studies on the melting and solidification of cast irons have involved the use of large scale melting operations. In studies that examine the effect of impurities on solidification behaviour two major difficulties are encountered. These are the difficulty of making additions to the iron, and the low yields of such additions.

A technique has been developed whereby these difficulties are largely overcome and the present communication describes this method in which accurately weighed, compacted powder samples are rapidly melted in an induction coil. The technique involves the use of high purity metal powders (electrolytic iron, spectroscopic grade graphite, and high purity silicon) which are weighed and thoroughly mixed. The resulting powder mixture is compacted to form a cylinder 1 cm in diameter under a pressure of approximately 25000 psi.

The compacted sample is placed under an inert atmosphere in an alumina crucible situated in a graphite susceptor and the whole assembly positioned in a high frequency (400 kHz) induction coil.

Temperature measurements are recorded continuously during melting and freezing using a thermocouple located at the base of the sample. Considerable alloying occurs in the solid state before fusion as the recorded melting tempera-

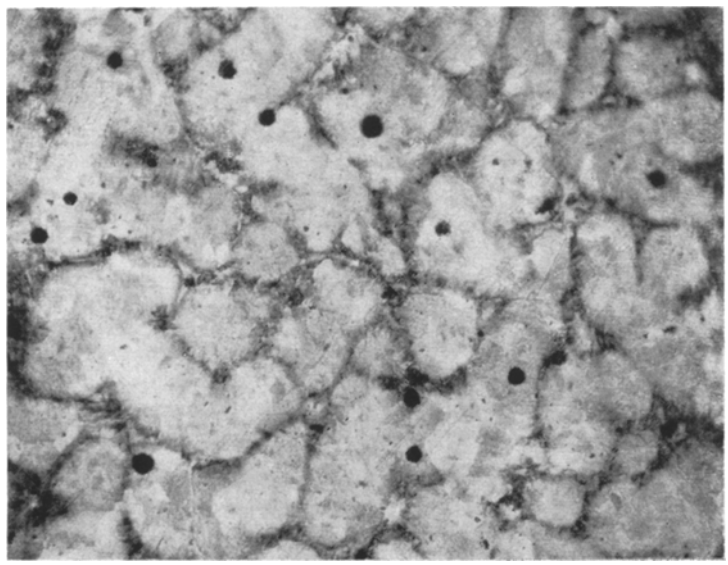


Figure 1 (a) Microstructure of an alloy of Fe-3% C-2% Si showing graphite present as nodules. Nital etch (× 200).