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Carbon Fibres from Mesophase Pitch [and Discussion]

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Carbon fibres from mesophase pitch

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[Plates 1 and 2]

Carbon fibres derived from mesophase pitch have been available as continuous filament tow or yarn since 1974. By comparison with other carbon fibres, they are of the high modulus, moderate strength type but are different from those of other precursors in that they are significantly higher in density and are 'graphitizable' in that they develop three dimensional crystalline order at high temperatures.

Recent progress toward elimination of structural flaws in both yarns and component filaments have resulted in improved levels of strength for fibres which possess a Young modulus of 380 GPa. Strand strengths of 2.4 GPa have been achieved and a still higher level appears to be a practical goal.

Carbon fibres from mesophase pitch are capable of achieving a high Young modulus with inexpensive processing techniques and should, therefore, be uniquely suitable for all 'modulus-critical' applications. Ultimately, they may also possess the capability of achieving extremely high tensile strengths.

Introduction

Low-cost, high modulus carbon fibres from a mesophase pitch precursor have been available in continuous filament form since 1974 (Volk 1974). Before that time, high modulus carbon fibres were available commercially only from rayon or polyacrylonitrile (PAN) precursors. Fibres from mesophase pitch are one of the least expensive high modulus carbon fibre products on the market. Recent improvements in processing have permitted a reduction in the incidence of fibre defects, with the result that strand strengths have been substantially improved. It is the purpose of this paper to describe how the control of defects has resulted in stronger fibres.

Process

The process for preparing carbon fibres from a mesophase pitch precursor (Barr *et al.* 1976; Singer 1977) is indicated below:

$$\begin{matrix}\text{commercial} \\ \text{pitch}\end{matrix} \longrightarrow \begin{matrix}\text{polymerize} \\ \text{to mesophase}\end{matrix} \longrightarrow \begin{matrix}\text{melt} \\ \text{spin}\end{matrix} \longrightarrow \begin{matrix}\text{thermoset,} \\ \text{e.g. air}\end{matrix} \longrightarrow \begin{matrix}\text{carbonize} \\ 1500\text{–}3000\ ^\circ\text{C}\end{matrix}$$

Petroleum or coal tar pitch is thermally treated to temperatures above 350 °C to convert it to a 'mesophase pitch' which contains both isotropic and anisotropic (liquid crystal phase) material. The mesophase pitch is melt spun through a multiple-hole spinneret to produce 'green' yarn. The yarn is made infusible by oxidation at temperatures below its softening point (to avoid fusing filaments together). It is then carbonized to temperatures normally around 2000 °C.

The main advantage of this process over the rayon or PAN precursor processes (Bacon 1973; Watt & Johnson 1969) is that no tension is required during processing to develop or maintain the molecular orientation necessary to achieve high modulus and high strength. Owing to the anisotropic liquid crystal nature of the pitch, molecular orientation is achieved in the spinning process and is preserved or enhanced throughout processing without the use of tension. A related advantage of this process is the high carbon yield in going from precursor fibre to carbon fibre: greater than 80% as opposed to 50% or less for other precursors.

Structure

In comparison with PAN-based carbon fibres, those made from mesophase pitch are characterized by a high density and a large 'crystallite' size (Bright & Singer 1978). Comparative data are given in table 1. These characteristics are a direct consequence of their liquid crystal origin which is shared with all 'graphitizing' carbons (Brooks & Taylor 1965). PAN- or rayon-based fibres, on the other hand, are examples of materials produced by charring of a resin that never passes through a liquid crystal state. This latter process leads to 'non-graphitizing' carbons or 'glassy' carbons.

Table 1. Typical structural data for commercial high modulus (*ca.* 380 GPa) carbon fibres from several precursors

precursor material	density/(g cm^{-3})	crystallite size, L_c/nm
mesophase pitch	2.02	15
PAN	1.86	6
rayon	1.70	5

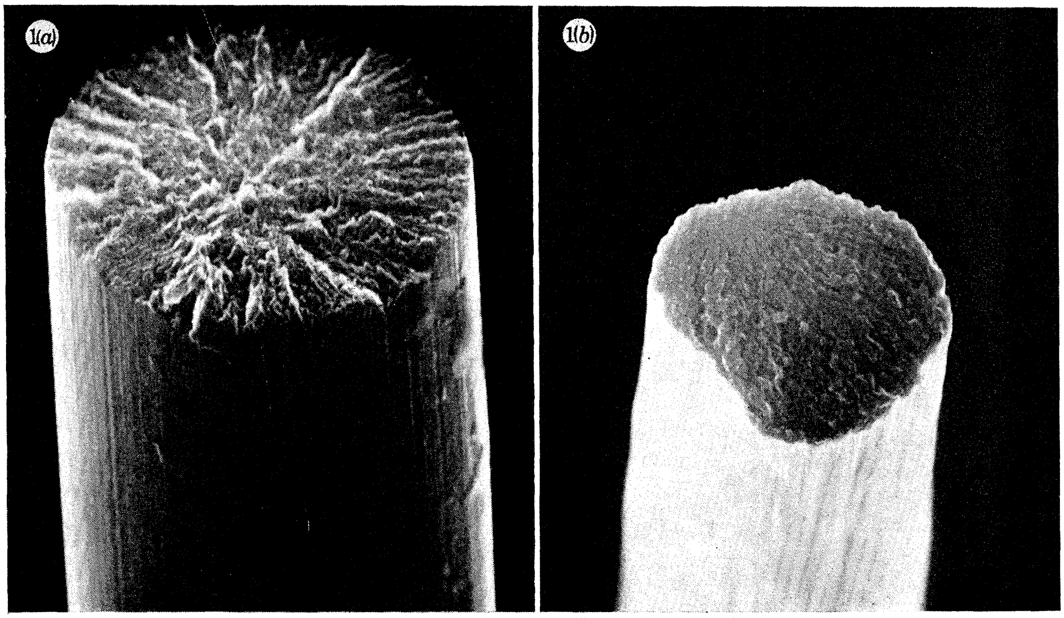
The coarser texture of mesophase pitch-based carbon fibres compared with that of PAN-based fibres can be seen in scanning electron micrographs of fracture surfaces (figure 1). The fracture surfaces of multifilament mesophase pitch-based fibres typically exhibit radial structure, although a nearly random orientation of basal planes in the cross section is also observed. On the other hand, in monofilament spinning, circumferential orientation is often seen (Barr *et al.* 1976). The same three classes of transverse structure have been observed in PAN precursor fibres (Knibbs 1971) but the circumferential structure seems to be most common.

Properties

The mechanical properties of current-day mesophase pitch-based carbon fibres are compared with those of several PAN-based fibres in table 2. Commercial mesophase pitch-based fibres possess a Young modulus of about 380 GPa. Fibres now in an advanced development stage possess strengths equal to those of most PAN-based fibres of comparable modulus; they will be significantly lower in price.

Strength-limiting defects

The major strength-limiting defects that have been found in mesophase pitch-based carbon fibres are (1) interfilament fusing; (2) internal voids; (3) foreign particle inclusions; (4) surface defects; (5) irregular cross-sectional shapes. These types of defects have all been found in



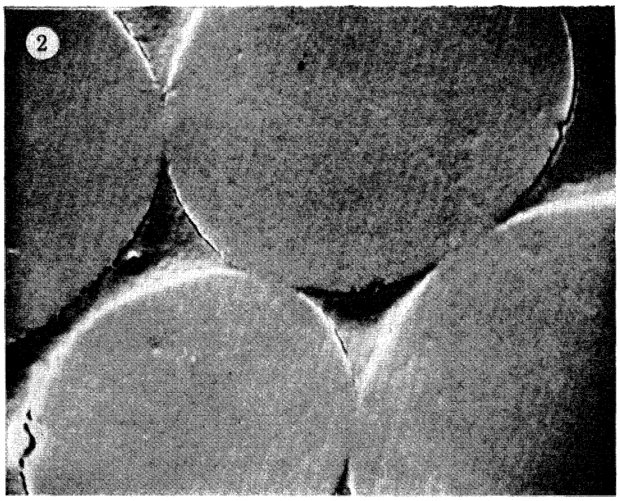


FIGURE 1. Fracture surfaces of high modulus carbon fibres. (*a*) Mesophase pitch fibre precursor. (*b*) PAN fibre precursor.

FIGURE 2. Fusing or bonding between carbon fibres.

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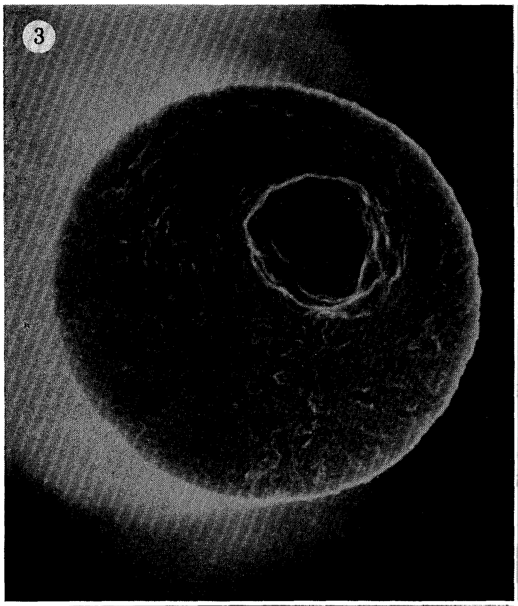

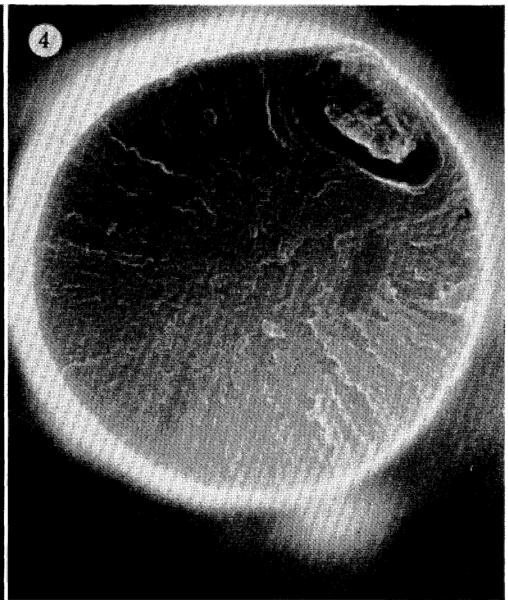

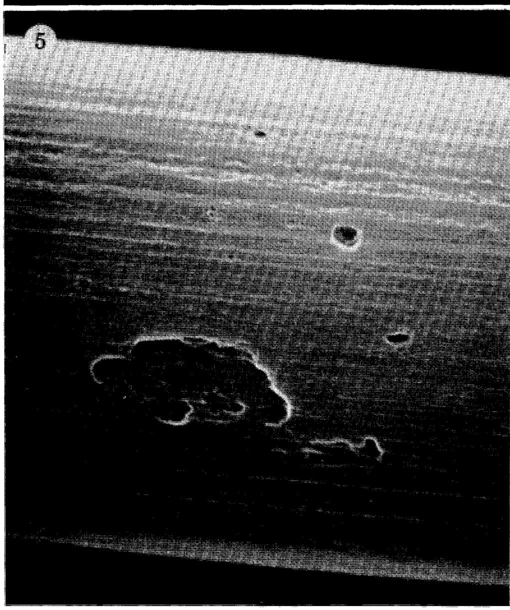

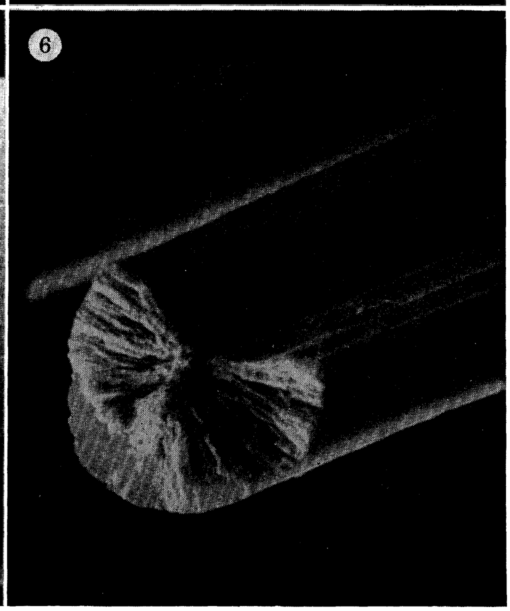

FIGURE 3. Internal void in carbon fibre.

FIGURE 4. Included particle in carbon fibre.

FIGURE 5. Surface defects on carbon fibre.

FIGURE 6. Carbon fibre containing a wide radial crack.

Table 2. Properties and prices of carbon fibres in the U.S. (approximate values)

number of filaments (1000s)	tensile strength/GPa	density/(g cm^{-3})	price/($ lb^{-1})
210–240 GPa modulus, PAN			
3	2.8	1.75	35
6–12	2.8	1.75	32
40	2.1	1.75	28
160	2.8	1.75	18+
340–380 GPa modulus, PAN			
3	2.4	1.80–1.85	125
6–10	2.3	1.80–1.85	90
40	2.4	1.80–1.85	*ca.* 50
380 GPa modulus, mesophase pitch			
2 (production)	2.0	2.02	20
2 (development)	2.4	2.02	20

carbon fibres from other precursors (Johnson & Thorne 1969; Sharp *et al.* 1974; Jorro *et al.* 1976); they have been studied most thoroughly in the case of PAN-based fibres.

Interfilament sticking or fusing can occur either in the precursor spinning process or during thermal processing. In either case, it results in brittleness of the yarn bundle and poor structure in the composite. Figure 2 shows a severe case of interfilament fusing in a mesophase pitch-based carbon yarn bundle.

Internal voids are caused by gas bubbles in the as-spun fibre or by evaporation of foreign matter during thermal processing. An internal void was identified as the strength-limiting defect in the filament shown in figure 3.

Foreign particle inclusions are normally due to contaminants in the original spun fibre. An example is shown in figure 4.

Surface defects can have a variety of causes. In most cases, the origin can be traced to fibre surface contamination or mechanical damage. An example of a fibre with surface defects is shown in figure 5.

An irregular cross-sectional shape of the individual filament represents a defect which may not always be strength-limiting. The evidence that they are strength-limiting is usually indirect. In the case of mesophase pitch-based carbon fibres, the most common irregular shape resembles that of a pie with a missing wedge (figure 6). In actual fact, the 'missing wedge' is simply a wide radial crack in the originally round fibre. In general, the cracked fibres are found to be weaker than uncracked, round fibres.

Strengths of 'clean' fibres

Chwastiak *et al.* (1978) have shown that carbon fibres prepared from *monofilament*-spun mesophase pitches exhibited very high strengths if special precautions were taken not to contaminate the pitch prior to spinning. At 20 mm test gauge length, these fibres exhibited strengths of 2.5 GPa, compared with only 1.5 GPa for 'ordinary' fibres. Through extrapolation to very short gauge lengths, it was suggested that 'intrinsic' strengths of flaw-free fibres might reach levels of 7 GPa. The Young modulus of the fibres of this study were in the vicinity of 200 GPa.

Efforts to reduce the incidence of flaws from *multifilament*-spun fibres, processed by commercial-scale processing techniques, have recently resulted in marked improvements in fibre strengths. For 2000-filament strands (impregnated with epoxy resin, cured, and measured at 250 mm gauge length), average strengths up to at least 2.4 GPa have been measured for fibres possessing a Young modulus of *ca.* 380 GPa. This level of strength is equal to that achieved in the best cases for commercial fibres of comparable modulus made from rayon or PAN precursors. A practical goal of 2.8 GPa or higher is believed to be attainable. These fibres are expected to be the best choice for most 'modulus-critical' applications for carbon fibre composites.

The author is grateful to J. B. Barr, S. Chwastiak, J. B. Jones, D. J. Menegay, and R. E. Smith, whose work in flaw analysis provided the micrographs for this paper and helped guide the efforts of many others of this laboratory.

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Discussion

G. F. Modlen (*Department o Engineering Production, Loughborough University of Technology, Loughborough, Leics. LE*11 3*TU, U.K.*). I should like to ask Dr Bacon two questions.

First: he referred to the two types of arrangement within the carbon fibres produced from the mesophase pitch – namely, the onion-skin and radial arrangements. Can these differences be ascribed to any corresponding differences in the way in which the mesophase flowed during formation of the precursor fibre?

Secondly: a previous speaker referred to the necessity for extension of any fibre in order to obtain satisfactory longitudinal molecular alignment – this presumably being due to some extent of relaxation of the orientation produced in the spinning process. Is it the case that the orientation of the pitch molecules with their planes parallel to the fibre axis produced by spinning, is not lost to any appreciable extent after spinning, and that subsequent extension of the fibre is, therefore, not required?

R. Bacon. To answer the second question first: yes, Dr Modlen has stated the case correctly.

Regarding the first question concerning the causes of radial as opposed to onion-skin structures in our fibres: yes, we believe the differences are related to the flow conditions during fibre formation, but we have not yet sorted out exactly what causes these differences. Some of the basic factors involved are discussed in a very pertinent way by Sir Charles Frank (see below).

SIR CHARLES FRANK, F.R.S. (*The H. H. Wills Physics Laboratory, Royal Fort, Bristol BS*8 1*TL, United Kingdom*). Professor Bailey has asked, 'What are the objects which are oriented in the flow of mesophase pitch?' I would answer 'no other objects than the molecules, but they are oriented collectively, not individually.' The orientation of each molecule in a mesophase is correlated with that of its neighbours, and this neighbour-to-neighbour correlation extends throughout the specimen. The idea of discrete pockets of similarly oriented molecules, called 'domains' or 'cybotactic groups' is outdated. The planes of large orientational change are not 'walls' dividing the space into discrete regions as these terms imply, but lines of disclination, around which orientation changes continuously and without interruption. One may define a correlation length, over which similar orientation persists, but to interpret it as the size of discrete pockets of similarly oriented molecules can be misleading.

I have not had recent contact with work on mesophase pitch, and things may have been learnt during the last two or three years which make what I say wrong, in which case Dr Bacon must correct me: I have supposed that the mesophase in question is a nematic, representing that long-sought class of nematics with platy molecules, so that the longest molecular dimensions are preferentially perpendicular to the director, rather than parallel to it as is the usual case, with nematics formed from rod-like molecules (for example, the nematic Kevlar solutions). The director should be distinguished from 'the direction of the molecules' as it is often loosely called; it is the symmetry axis of the orientational distribution function for any molecular direction.

The main hydrodynamic effect on molecular orientation comes from the longitudinal velocity gradient which operates in the convergent flows at approach to the orifice and in the free stream after exit from the orifice, and a secondary hydrodynamic effect depends on the radial velocity gradients which are strongest in the die itself. In the mesophase pitch, unlike most nematics, the convergent flow sets the director perpendicular to the flow direction, so that the planes of the molecules are parallel to the fibre axis. Then two distinct viscosities affect the transverse velocity gradient: that for simple shear on a plane perpendicular to the director (or for simple shear on a plane parallel to the director, with motion also parallel to it, which is the same), and that for shear on a plane parallel to the director with motion orthogonal to it. Which of these two is the larger may determine the preference between what have been described as radial and onion-skin textures (director in circles around the plane axis, or radial, respectively). The ratio of these two viscosities will be expected to change with molecular weight and with temperature. Again, in these fibres of dimensions of micrometre order of magnitude, the surface exerts a strong control over orientation. It is from the interplay of these factors that we may expect to interpret texture variations, and core and sheath structures, in mesophase pitch fibres.

B. MCENANEY (*School of Materials Science, University of Bath, Bath BA*2 7*AY, Avon, U.K.*). Dr Bacon mentions in his paper that, in contrast to PAN-based carbon fibres, mesophase pitch based carbon fibres develop three dimensional graphitic character upon heat treatment to 2500–3000 °C. Is it possible, as a consequence, that shear mechanisms become significant in deformation and failure of high temperature mesophase-based carbon fibres?

R. BACON. Yes. As Dr Reynolds points out in his paper, shear mechanisms are important even in relatively low temperature PAN-based carbon fibres. In more 'graphitic' fibres, such as high temperature mesophase-based carbon fibres, they are expected to be exceedingly important in deformation and failure mechanisms.

T. H. BLAKELEY (26 *Avon Castle Drive, Ringwood, Hampshire RH*24 2*BB, U.K.*). The speaker has referred to 'pitch' without qualifying this in any way. Presumably he refers to a pitch from coke oven crude tar; but the characteristics of such pitches can vary substantially according to the rank of the original coal and the heat treatment suffered in the carbonization of the coal. Am I right in thinking that a highly aromatic pitch – i.e. one from high-rank coal carbonized in moderately severe thermal conditions – is the one which would be preferred for the interesting developments described by the speaker?

R. BACON. As Dr Blakeley has suggested, highly aromatic, so-called 'graphitizing' pitches, derived either from coal or petroleum, can be used for these fibres.

G. MANFRE (*Centro Ricerche Fiat, Orbassano, Italy*). In Dr Bacon's lecture, among the advantages shown of the pitch carbon fibres in comparison with the PAN carbon fibres there are: (*a*) no tension during carbonization, (*b*) 80% yield, (*c*) fast process in carbonization.

(*a*) Since it is a melt spinning one must have tension during the attenuation diameter of the forming fibre.

(*b*) 80% yield is not very much related to the cost of the fibres. In fact, owing to the pretreatment of the pitch as a precursor there is not significant difference between pitch and PAN in comparison with the final cost of the fibre.

(*c*) I do not understand how a spinning molten technology can be very high in productivity in comparison with the wet spinning. So owing to the fact that the final steps, carbonization and graphitization are the same, it is difficult to understand how the cost of pitch-based carbon fibres can be less than the PAN-based carbon fibres as you assessed, especially since the PAN fibre can be wet spun in very large filament tows, for example, 90000 fibres from one spinneret.

R. BACON. (*a*) Of course, tension is required during the attenuation of fibre diameter in all fibre drawing processes. My point was that no tension is required during carbonization of the already formed precursor fibre.

(*b*) 80% yield of carbon fibre from the precursor fibre is clearly an advantage for pitch over the 50% yield that is obtained with PAN fibre. If the costs of pre-treated pitch and of PAN are comparable, and if spinning costs are comparable, then this difference in carbonzation yield becomes the dominating factor in the relative costs.

(*c*) Melt-spinning technology is, of course, commonly used in high-productivity textile industry (glass, nylon, polyester, polypropylene) and is often preferred over wet spinning for its simplicity. No solvent is required, and hence problems of solvent recovery and waste water purification are avoided.

As Dr Manfre has pointed out, large tows containing many tens of thousands of filaments may be more economically produced by wet-spinning, and carbonization costs may be lower. The present carbon fibre market does not use these heavy tows to any great extent, the demand being primarily for prepreg tape, filament-wound bodies, and cloth laminates. This situation may, of course, change.

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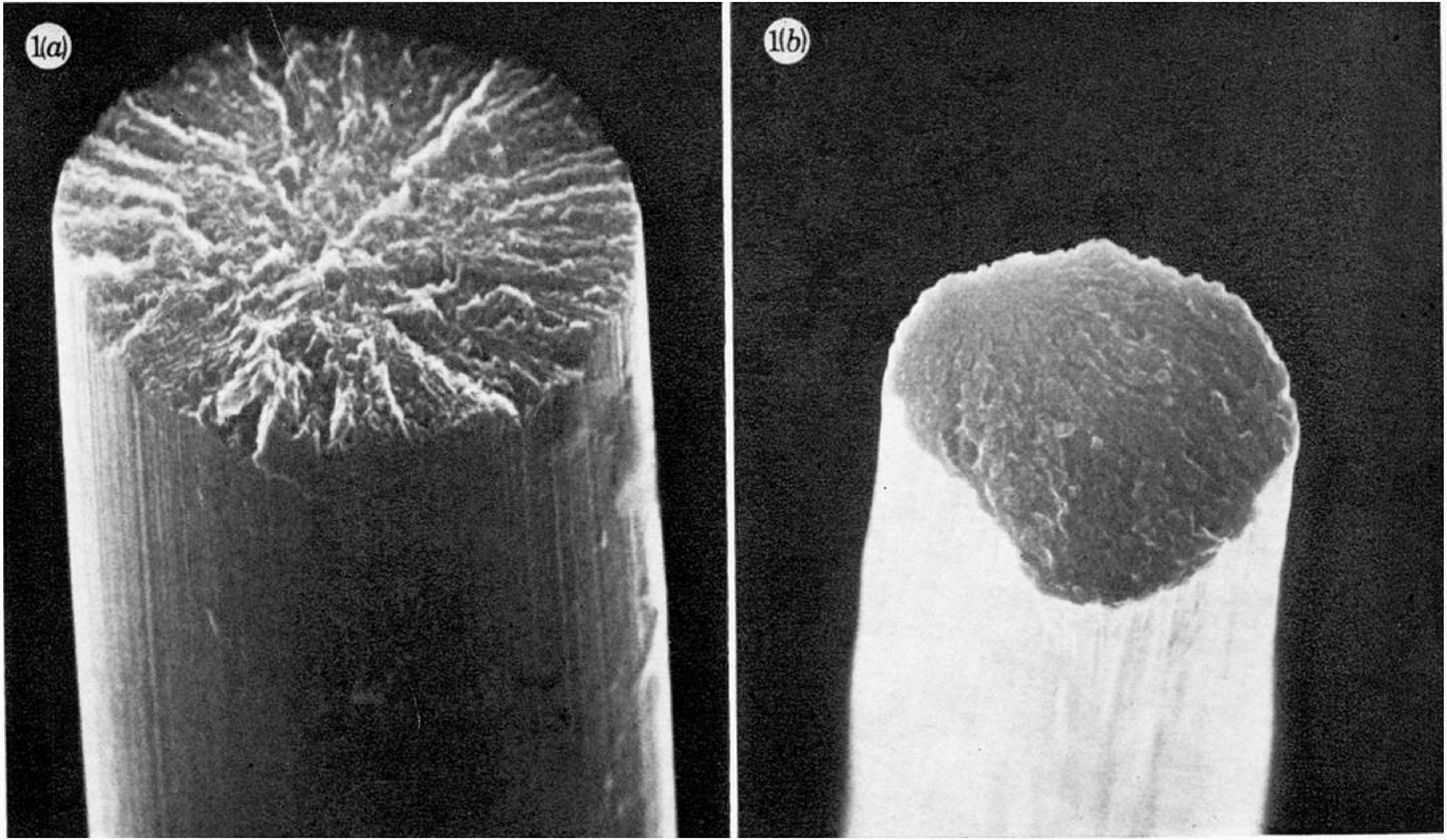

FIGURE 1. Fracture surfaces of high modulus carbon fibres. (*a*) Mesophase pitch fibre precursor. (*b*) PAN fibre precursor.

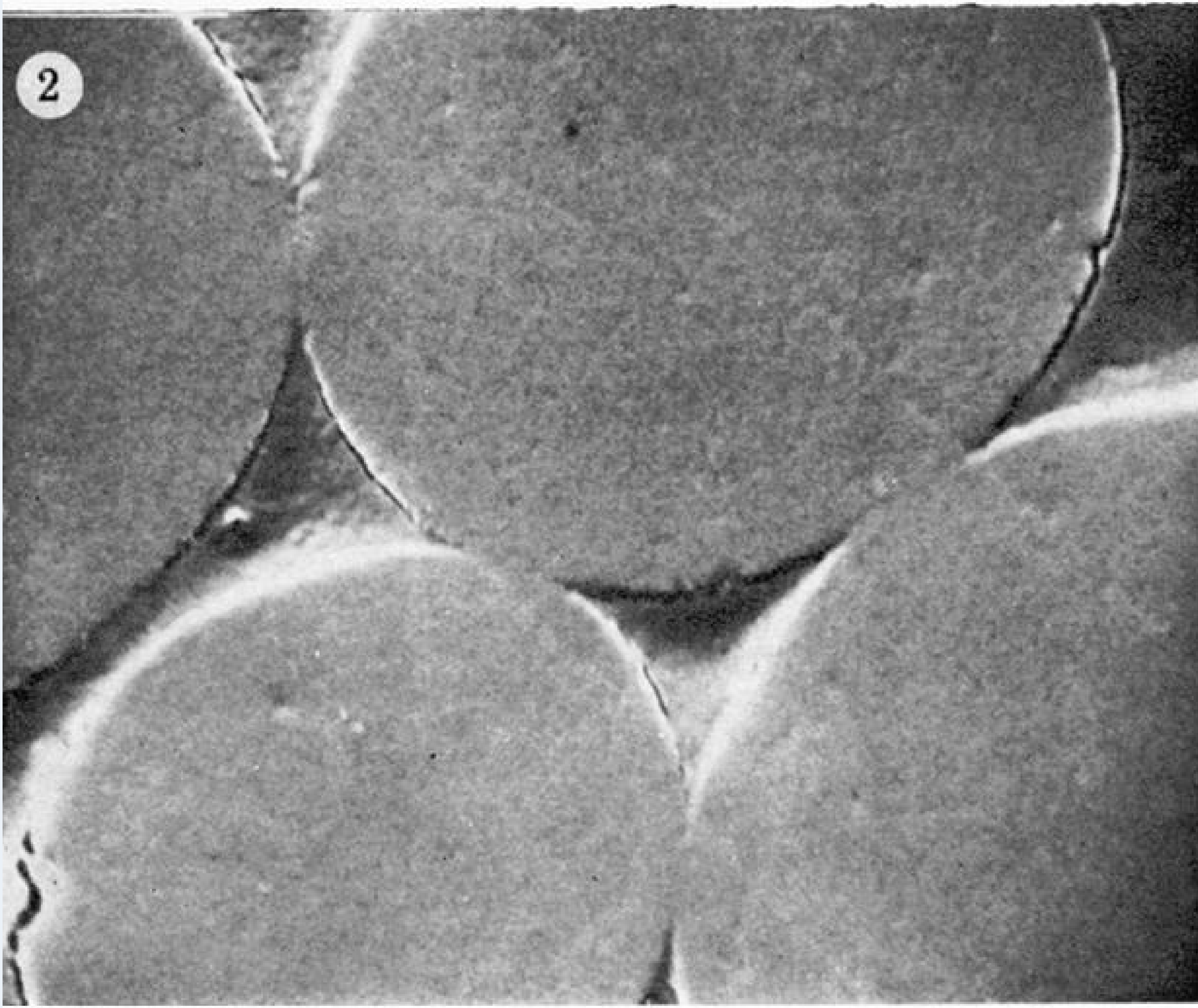

FIGURE 2. Fusing or bonding between carbon fibres.

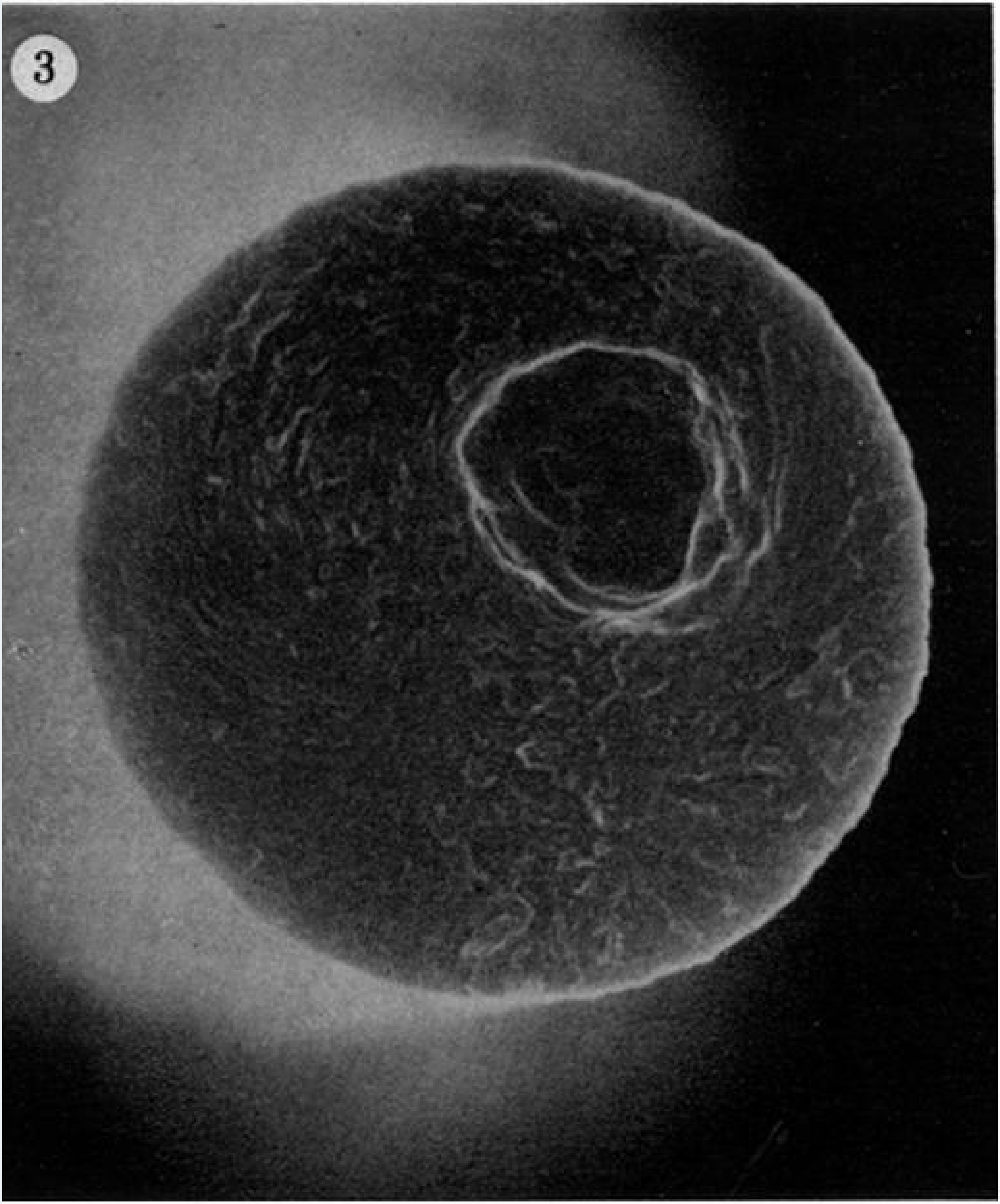

FIGURE 3. Internal void in carbon fibre.

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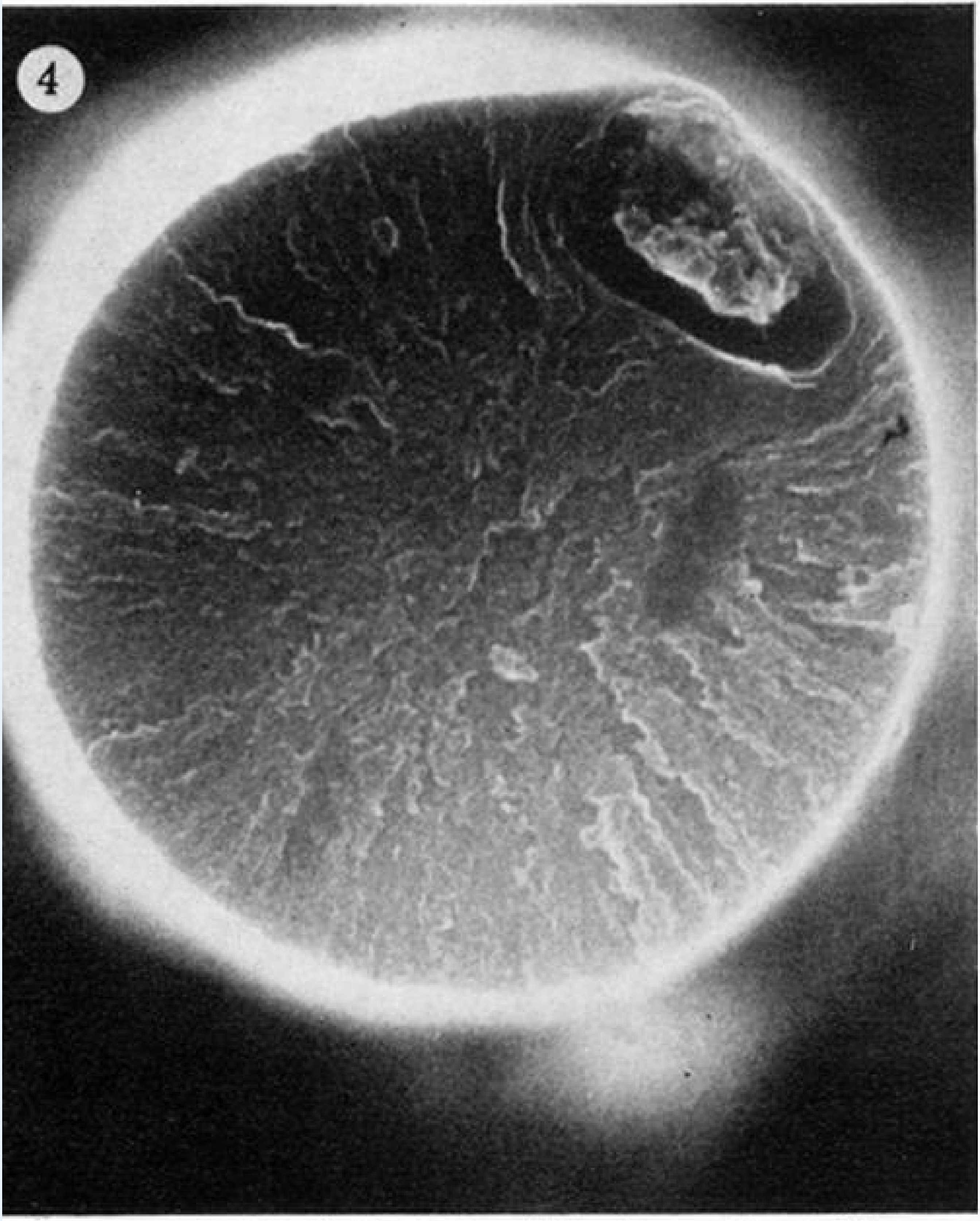

FIGURE 4. Included particle in carbon fibre.

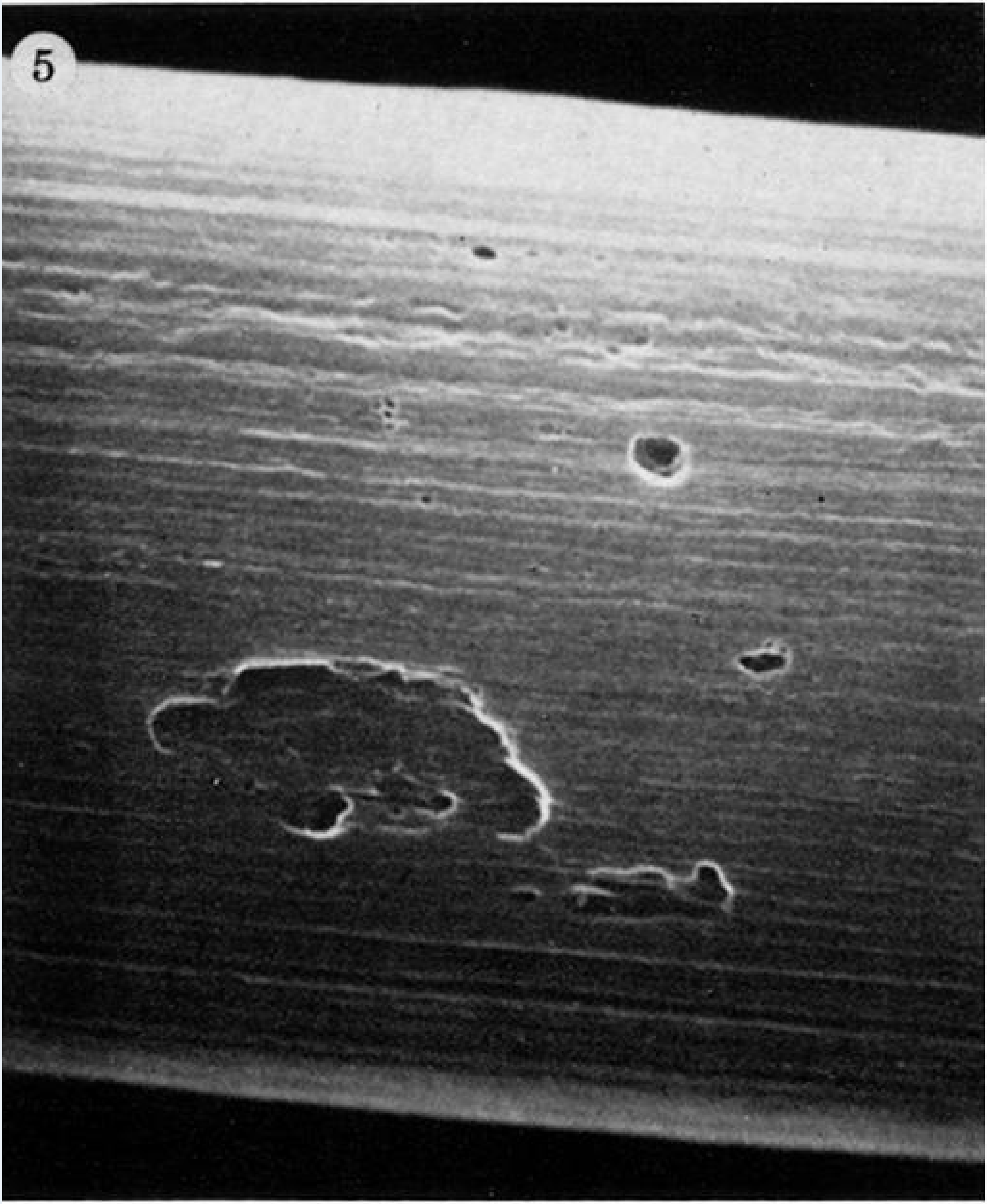

FIGURE 5. Surface defects on carbon fibre.

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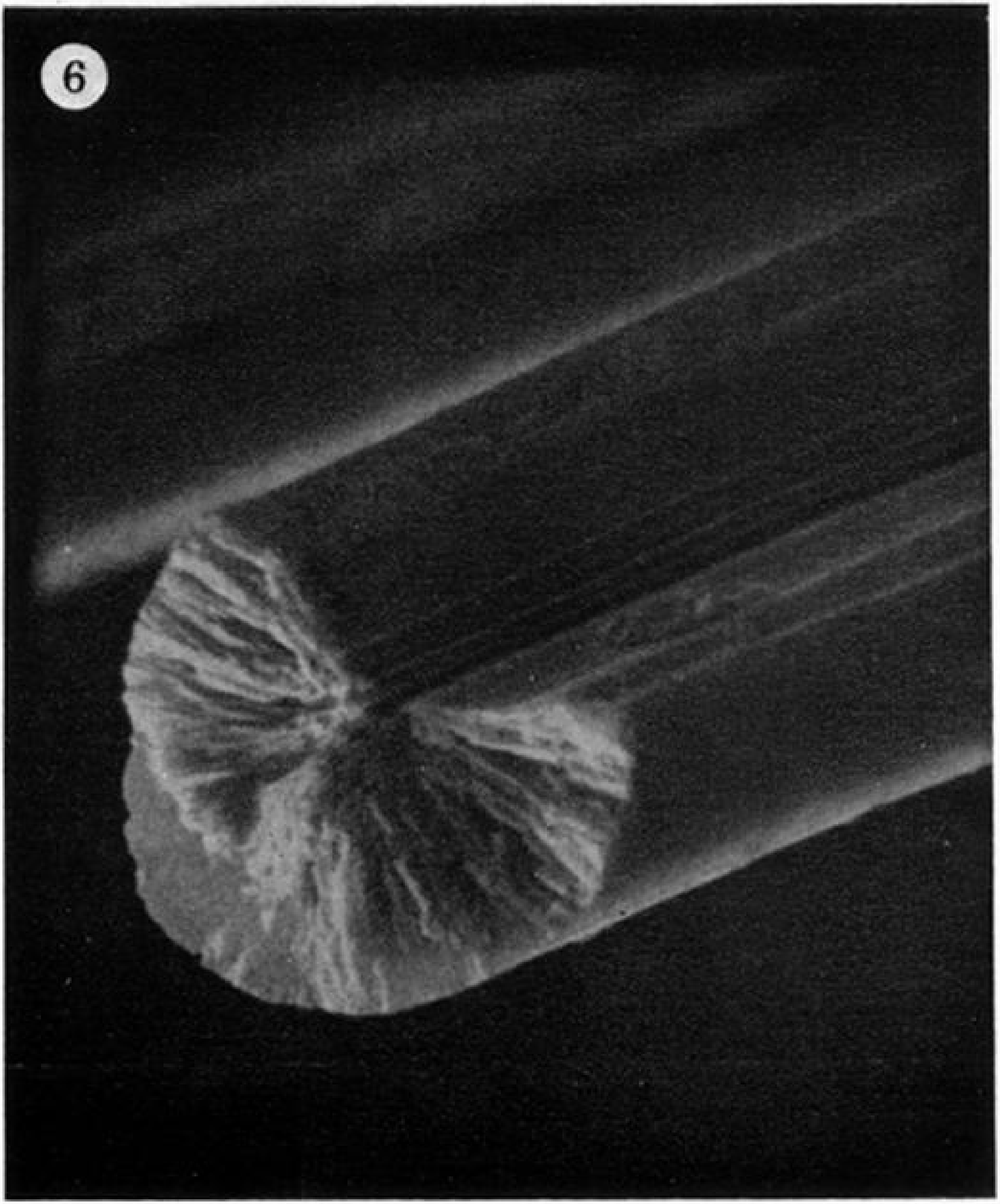

FIGURE 6. Carbon fibre containing a wide radial crack.

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