JOURNAL OF MATERIALS SCIENCE 28 (1993) 2337–2346

Glass fibres with fine conducting cores

J. D. AYERS
Physical Metallurgy Branch, Naval Research Laboratory, Washington, DC 20375, USA

New methods are described for producing glass fibres containing single or multiple metallic filaments along their axes. The new processes are based upon that first described in 1924 by Taylor. His method consisted in melting a small amount of metal within a glass capillary and of then drawing a fibre from the softened glass. Fibres containing single, submicrometre diameter metal or semiconductor filaments are prepared by inserting a composite fibre prepared by Taylor's method in a glass capillary and drawing from this assembly a new fibre in which the diameter of the axial filament is reduced in proportion to the ratio of the diameters of the capillary and the new fibre. This method has produced filaments substantially less than 1 μm diameter. The second new process consists in drawing a fibre from a tube filled with a mixture of metal and glass powders. This method can produce fibres containing hundreds of filaments within any given cross-section. The filaments are of limited length, however, and they have a spectrum of diameters which depend on the powder particle-size distribution and the processing conditions. They typically range from a few micrometres in diameter down to a fraction of a micrometre.

1. Introduction

Taylor's original fibre-drawing method [1] provides a remarkably simple way of making short lengths of fine conducting filaments. By employing small-diameter glass capillaries and pulling them quickly so as to reduce them to fine diameters before the glass cooled below its working temperature, Taylor produced fibres as small as 1 μm diameter and the filaments contained within them were even finer. He had no direct means available for measuring the diameters of the filaments, but he was able to establish electrical contacts with some of the filaments and measure their resistance. Assuming that the filament had the same resistivity as the bulk metal, he calculated that one antimony filament was only 0.2 μm in diameter. Apparently, no subsequent effort has succeeded in producing finer filaments than those made by Taylor, but considerable research has been devoted to developing methods for producing these materials in long lengths and to characterizing the properties of the metal filaments produced by the various versions of the process. Much of this effort is discussed in a recent review by Donald [2].

In honor of Taylor's invention, glass fibres containing metallic filaments are frequently called Taylor wires. Those with micrometre-scale conducting filaments are called microwires by some researchers. This paper will employ the former terminology. Much of the research on methods for producing Taylor wires has employed induction heating to melt a small metal pool in the closed end of a glass tube, the tube being advanced into the heating coil during drawing of the fibre to make up for the glass withdrawn. When very long lengths are desired, a metal wire can be fed into the tube to maintain a constant volume of molten metal within it [3,4]. With suitable refinements, such methods can produce multikilometre lengths of fibre, but minimum filament diameters are generally greater than 1 μm [4,5].

One limitation of the various versions of the Taylor process is that if special care is not taken, shrinkage of the metal core during solidification will cause the filaments to be broken up into short sections. Similarly, expansion of materials such as bismuth during solidification can cause splitting of the fibres. These problems can be avoided by quenching the fibre during pulling, so as to maintain the solid/melt interface near the melt pool, thus permitting melt to feed to or from the melt interface to make up for the shrinkage or expansion [6]. If fine metal filaments are desired, the fibre must be pulled at high velocities, and quenched very near the hot zone to maintain the solid/melt interface sufficiently near the melt pool to permit feeding of the additional liquid to the solidification front [4]. The new processes described here do not permit melt-volume adjustments, so most of the metal filaments produced have breaks along their length. Long break-free filament lengths have, however, been produced by both methods with materials which expand upon solidification.

2. Fibre processing

Three general types of fibre-processing techniques are discussed here. These are: (1) methods similar to those of Taylor for making fibres with single filaments, (2) the multiple drawing method, which employs the first type of fibre, and (3) the multifilament method.

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2.1. Processing of Taylor wires

Taylor wires for use in the multiple-drawing process are made by two different methods. One of these methods is very similar to that described by Taylor in his 1931 patent [6]. It consists of mounting a glass capillary filled with a powdered metal or alloy in a glass lathe which rotates the capillary at about one revolution per second. The end of the capillary is heated with the flame from an oxygen–hydrogen torch, and fibres are drawn from the heated end at rates of up to 4 m s^{-1}. In order to prevent the entrapment of gas bubbles in the core of the fibre, the capillary is evacuated by means of a mechanical vacuum pump which is connected to the capillary through a rotary motion vacuum feedthrough. The drawing apparatus is equipped so that the fibre can be quenched by pulling it through a pool of water located only about 1 cm from the oxygen–hydrogen flame. This quenching makes possible the formation of some filaments which are continuous over lengths of many metres. This process has been used to draw fibres of several glasses, including SiO_2.

The second variation of the Taylor process employed in this study is shown schematically in Fig. 1. This process employs radiant heating to soften the glass and melt the metal. The radiant heat is supplied by an SiC susceptor ring which is inductively heated by a 3 kW, high-frequency generator. The SiC susceptor has an outer diameter of 33 mm, an inner diameter of 15 mm and a length of 12 mm. The SiC ring is maintained at constant temperature by sensing its temperature with an infrared detector whose output controls the power of the high-frequency generator. During any given experiment the temperature is stable to within about 10 °C, but the temperature indicated by the infrared detector was found to be unreliable. Any process temperatures recorded are, therefore, only approximate. Because the SiC susceptor will not withstand temperatures above about 1600 °C, this process variation cannot be used with SiO_2 glass.

When fibres containing metal filaments are made by the method illustrated in Fig. 1, they generally exhibit breaks which result from shrinkage of the metal during solidification. Fibres containing copper filaments free of such breaks were prepared by pulling them at rates of only a few centimetres per second so as to permit melt from within the unreduced portion of the capillary to feed to the solidification interface. Pulling of germanium- and bismuth-containing fibres at similar rates prevented splitting of the fibre when the core material expanded upon solidification. Breaks or fibre splitting have been prevented with some filament materials by quenching the fibre with water as it leaves the SiC susceptor, but quenching is less successful than with the first process variation, because the water is located further from the hot zone. A greater standoff (about 2 cm) is needed to prevent cooling of the susceptor.

Efforts were made to produce fibres with submicrometre filament diameters by employing an experimental apparatus similar to that shown in Fig. 1, but in which the capillary contained a thin wire of copper or gold rather than metal powder. When the experiment was done with 76 μm diameter copper wire, the glass collapsed around the wire as intended, but when the wire melted in the region where rapid diameter reduction occurs, the thin melt column was unstable and broke down via mechanisms similar to those described by Rayleigh [7], into a series of spheres with diameters of several hundred micrometres. Similar results were seen with finer wire cores. Further attempts to produce submicrometre filaments employed the approach described below.

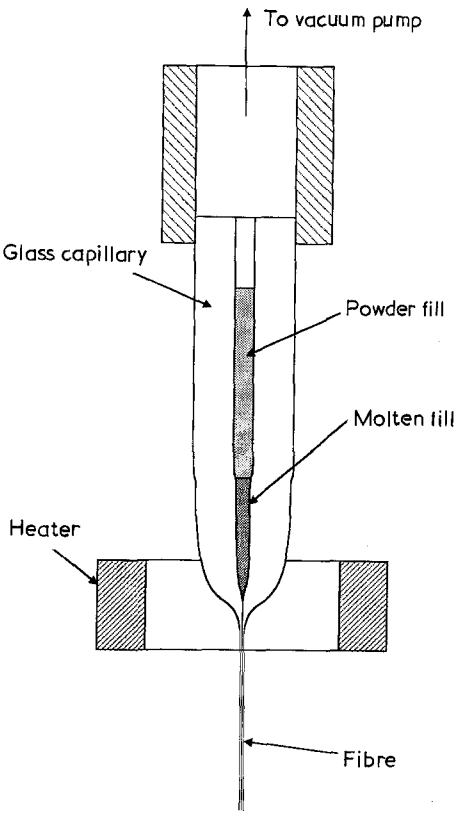

Figure 1 Schematic illustration of the process for the pulling of Taylor wires from a glass capillary filled with a powdered metal.

2.2. Repeated-drawing method

This method is based on a suggestion by Nagel [8] that fibres containing filaments finer than those prepared by Taylor could be made by inserting a Taylor wire into a thick-walled glass capillary and drawing a new fibre from the assembly. If all went as expected, the metal filament would experience the same diameter reduction as the glass. As an illustration of the potential of this approach, if the filament within the initial Taylor wire had a diameter of 3 μm, and the assembly were drawn with a reduction ratio of 300:1, then the resulting fibre would contain a filament only 0.01 μm in diameter. This method can be made to work, but great care is necessary because, when the glass is softened by heating, the surface energy of the initial metal filament causes the filament to break down, as did the wires in the experiments described above, into a series of small spheres. Subsequent drawing of the glass causes these spheres to be drawn out into filaments, but they are relatively coarse.

It has been found that the spheration problem can be prevented in some circumstances by using two

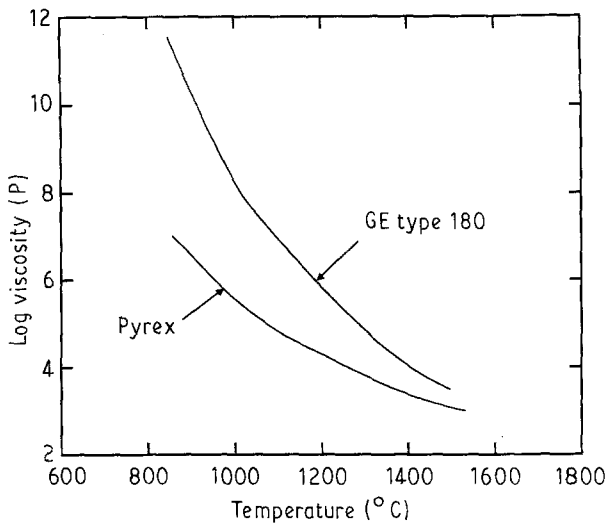

Figure 2 Temperature dependence of viscosities for glasses employed. Curves are reconstructed from data sheets supplied by manufacturers.

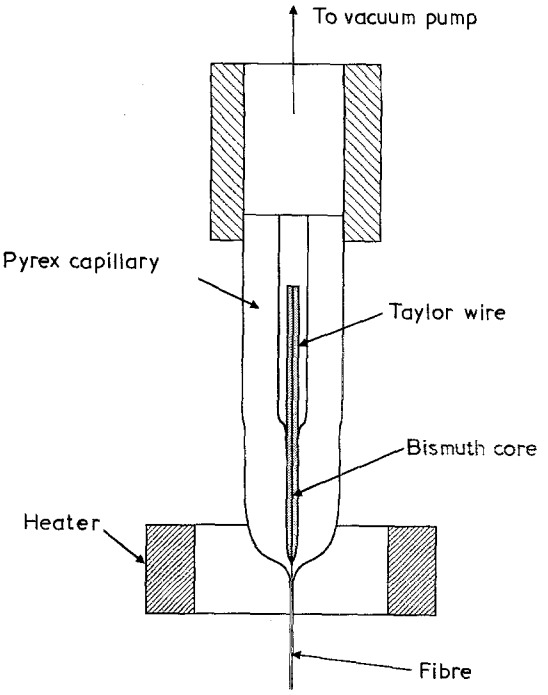

Figure 3 Schematic illustration of fibre drawing from a glass capillary containing a Taylor wire.

different glasses, one of which has a substantially higher working temperature than the other. A Taylor wire is first made using the higher working temperature glass, and this wire is then placed in the second glass and a fibre is pulled at a lower temperature. The rationale for employing the two different glasses is based upon exploiting the viscosity behaviour of glasses illustrated in Fig. 2. This figure shows the elevated temperature viscosities of Pyrex and General Electric type 180 glass, two glasses which have been found to work well with one another in executing the new process. Pyrex is a borosilicate glass, made by Corning, which has a low expansion coefficient and a high softening point. (The softening temperature of a glass is conventionally defined as the temperature at which its viscosity falls to $10^{7.6}$ P. The working temperature is defined as the temperature at which the viscosity equals 10^4 P.) The GE type 180 glass is an aluminosilicate grade of low alkali content which has the highest softening temperature of any commercially available glass other than Vycor and fused quartz.

When employing these two glasses, a Taylor wire of the type 180 glass with a metallic core is placed in a thick-walled capillary of Pyrex which has a closed lower end, and a new fibre is drawn under conditions which heat the glass to temperatures in the interval 1000–1100 °C. One can see from Fig. 2 that in this temperature range the GE 180 glass has a viscosity of 10^7 P or more, a viscosity which is sufficiently high that the inner glass could normally be deformed only very slowly. When the composite fibres are drawn, however, the relatively thick Pyrex, which can be drawn readily at these temperatures, imposes a triaxial stress on the inner glass which causes it to be drawn out uniformly at the same rate as the Pyrex. The 180 glass, in turn, causes the conductive core to be drawn out, and the high viscosity within the 180 glass sheath prevents the surface energy-driven breakdown of the metallic filament into spheres. The degree of stability against this spheration is sensitive to the thickness of the sheath, and stability of the filament has been improved by placing the Taylor wire in a fine (2 mm diameter) type 180 glass tube before inserting it in the Pyrex capillary.

During this second drawing operation, the capillary is evacuated so that as the outer glass is softened and it collapses into intimate contact with the Taylor wire, as illustrated schematically in Fig. 3. The composite fibres can be drawn at high rates and spooled, or they can again be drawn slowly, in preparation for yet another drawing operation. The rapidly drawn fibres normally have diameters of 100 μm or less, and their filamentary cores may then have submicrometre dimensions. Fibres can, of course, be drawn to much smaller diameters, but this normally requires that the glass be heated to temperatures which facilitate breakdown of the filaments into spheres. When the composite fibres are drawn at slow speeds, they typically have dimensions of a few tenths of a millimetre and their conductive cores are of the order of a micrometre in diameter. This second slow-drawing operation has been found necessary to prevent splitting of fibres containing germanium or bismuth, which both expand upon solidification. Truly fine filaments of these elements can be produced by inserting the doubly drawn fibres in a Pyrex capillary and drawing them a third time. This third drawing operation can be done at high speeds with no danger of splitting the fibre, but particular care is necessary to avoid overheating the glass during drawing because the driving force for spheration varies reciprocally with the filament diameter, and hence the break-up rate increases dramatically when the filaments have dimensions in the micrometre range prior to drawing.

The composite nature of fibres produced by the multiple drawing process can be discerned in Fig. 4. The lower magnification view, (a), shows the cross-section of a fractured fibre which was produced by a

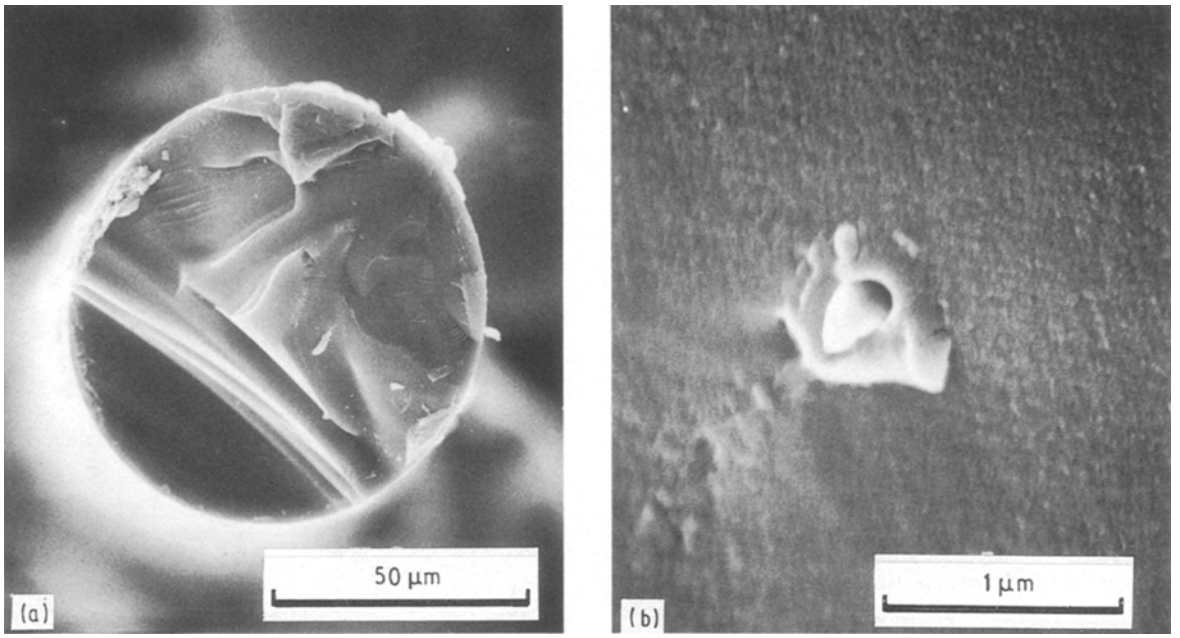

Figure 4 (a, b) Scanning electron micrographs of a fractured fibre end. (b) Higher magnification showing a bismuth filament protruding from a hole in the centre of the fibre.

three-stage drawing process. Fig. 4b shows the central region of the fibre at higher magnification, and in this view the fractured and highly deformed end of the bismuth core can be seen. Surrounding the bismuth core is a ring approximately three times as large, which is the type 180 glass used to draw the initial Taylor wire. The glass fibre is approximately 84 μm in diameter and the bismuth core has a diameter of 0.22 $\pm$ 0.02 μm. Syncrotron radiation studies [9] have shown that the filament pictured in Fig. 4b has the normal Bi-I crystal structure and that a single crystallographic orientation persists over lengths of at least 300 μm.

The diameter of the filament pictured in Fig. 4 was determined by measurements from the scanning electron micrographs and also by calculation, using the dimensions of the glass and bismuth core before drawing, the fibre diameter after drawing, and assuming conservation of matter. The computed diameter was within 10% of that observed. The same method has been used to calculate the diameters of filaments drawn from composite assemblies containing finer bismuth cores. By appropriate selection of initial core diameter and processing conditions, virtually any desired final filament diameter could be achieved. It came as a great surprise that the filament pictured in Fig. 4 and ones substantially smaller than it could be observed by optical microscopy. Filaments shorter than a wavelength of light do not, of course, produce sharp images, but the opaque core does produce a refraction effect which permits one to determine if the filament is present. This phenomenon is illustrated in Fig. 5, which shows the appearance at 577 times magnification of a segment end of a filament with a calculated diameter of 98 nm. The filament is present on the right-hand side of the image, but not at the left. Absence of the filament on the left-hand portion of the figure demonstrates the fact that even though the bismuth expands upon solidification, the filaments

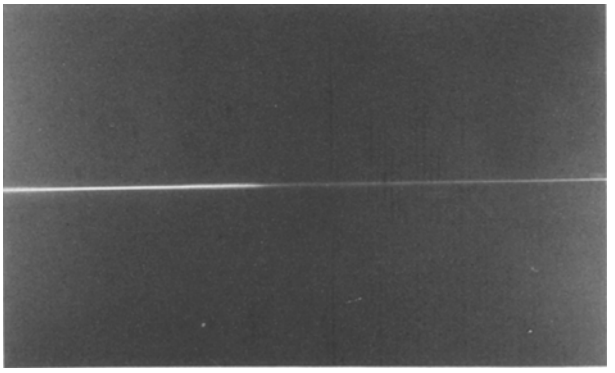

Figure 5 Optical micrograph of the refraction effects produced by a bismuth filament with a calculated diameter of 98 nm.

produced by this multistep-drawing process were broken into short lengths. These breaks are discussed in the next paragraph. The refraction effect apparent in that portion of Fig. 5 where no filament was present was produced by the empty core in the glass and by the difference in index of refraction of the thin shell of 180 glass surrounding the core from that of the Pyrex in the remainder of the fibre. The apparent diameter of the filament in Fig. 5 is substantially larger than the true filament diameter because it shows not the filament itself but a perturbation in the wave front of light illuminating the filament.

It can be seen in Fig. 5 that the refraction effect does not present a sharp image of the filament end, but does permit the end to be located to within about a micrometre. This refraction effect made it possible to measure the length of filament segments and approximate the break lengths of filaments with calculated diameters as small as 42 nm. Study of the fibre containing these 42 nm diameter filaments showed that some of the filament segments were as long as 15 mm. The longer filament sections thus had length-to-diameter ratios of approximately 3.6×10^5.

The breaks in these fine filaments result from the volume change during melting of the bismuth and differences in the thermal expansion coefficients of the liquid bismuth and the glass. When an initially continuous bismuth core is heated during the final drawing process, the metal contracts upon melting, creating short breaks at irregular intervals, and, as the composite is heated up to the drawing temperature, the molten bismuth expands more than the glasses containing it. For this reason, the pores produced during melting of the bismuth are closed before the drawing temperature is achieved, and the more rapid expansion of the bismuth at higher temperatures causes the glass to be plastically deformed. This deformation is not recovered during cooling, so the resultant filaments have the observed breaks. Measurements of the sums of the break lengths along multi-centimetre lengths of bismuth filaments with calculated diameters of 42 and 67 nm gave void fractions of 5.7% and 6.4%, respectively. These measurements show that, for the two glasses employed, the expansion of the bismuth upon solidification is less than the differential expansion above the melting point by about 6%.

Examination of the tapered end of the glass capillary from which the fibres were drawn showed no evidence of any tendency for the bismuth core to bead up at the drawing temperature, so there appears no reason to doubt that the observed refraction effect gives credible evidence of the presence of filaments with diameters less than one-tenth the wavelength of light. Filaments have been produced with calculated diameters as small as 20 nm, but no evidence of these could be observed with the optical microscope. While no confirmation of the existence of the finest filaments has yet been established, X-ray diffraction results have been obtained from filaments with calculated diameters as small as 42 nm [9]. Studies of multiply-drawn fibres are further discussed in Section 3.2.

2.3. Multifilament process

Fibres containing many parallel filaments are easily produced by filling a glass tube with a mixture of metal powder and crushed glass and by pulling a fibre as illustrated in Fig. 6. As in the processes described above, the external heat source softens the glass and melts the metal, but, in this process variation, isolated droplets of metal are drawn out into separate filaments. The applied vacuum helps to prevent excess porosity in the fibre by removing air and volatile constituents such as air and water vapour and by allowing atmospheric pressure to assist in collapsing the tube and compacting the fine, softened glass particles into a denser medium.

As an illustration of the results which can be achieved with the process, a 10 mm outside diameter Pyrex glass tube with 1 mm thick walls was filled with a mixture of crushed Pyrex and crushed germanium. Both of the powders were screened to remove particles larger than 63 μm. The blended powder charged into the glass tube contained 32% by weight of germanium. Fibres were pulled with the inductively heated SiC ring being held at a series of temperatures. It was found that the greatest number of germanium filaments was produced with a processing temperature just sufficient to permit the drawing of fibres. This temperature was believed to be near 950 °C, because at lower temperatures the germanium did not melt. One fibre drawn under such conditions is illustrated in Fig. 7. This figure shows a fracture cross-section through the fibre in Fig. 7a and an enlarged view from part of its core in Fig. 7b. In Fig. 7a the relatively featureless outer perimeter resulted from drawing of the glass tube used to contain the powder, and the inner portion contains the filaments. The bright, circular features in Fig. 7b are the ends of fractured filaments, and the dark circular and oval features are pores which resulted from incomplete sintering of the crushed glass. Fig. 7 demonstrates that, in this portion of the fibre, none of the filaments had diameters greater than 2 μm. That the germanium filaments are very long in relation to their diameters can be seen by examination of Fig. 8. These scanning electron micrographs show portions of a fibre which was etched to remove much of the glass. Fig. 8a shows a region of the fibre where etching had removed all of the outer glass sheath on one side of the fibre, exposing the filaments, but in which remnants of the sheath persisted on the other side of the fibre. This view demonstrates that most of the filaments persist over the full image width, and examination in the microscope showed that most had lengths in excess of a millimetre. Fig. 8b shows a portion of the fibre where the etching removed all of the glass except that in a small core region. The fibre was cut with a razor blade at the position pictured after it had been etched and cleaned. This view demonstrates that even the finest filaments are continuous

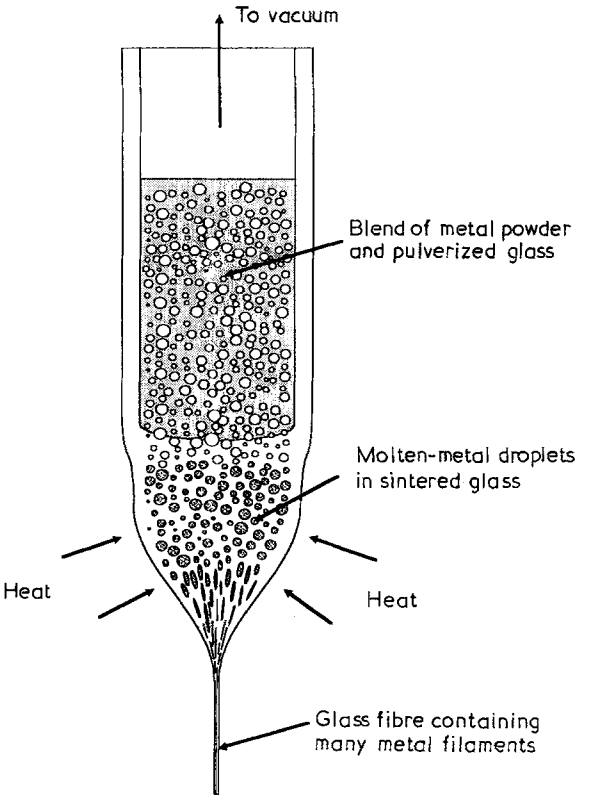

Figure 6 Schematic illustration of the process for making fibres containing many filaments. The pulverized glass fuses into a nearly continuous matrix which isolates the filaments.

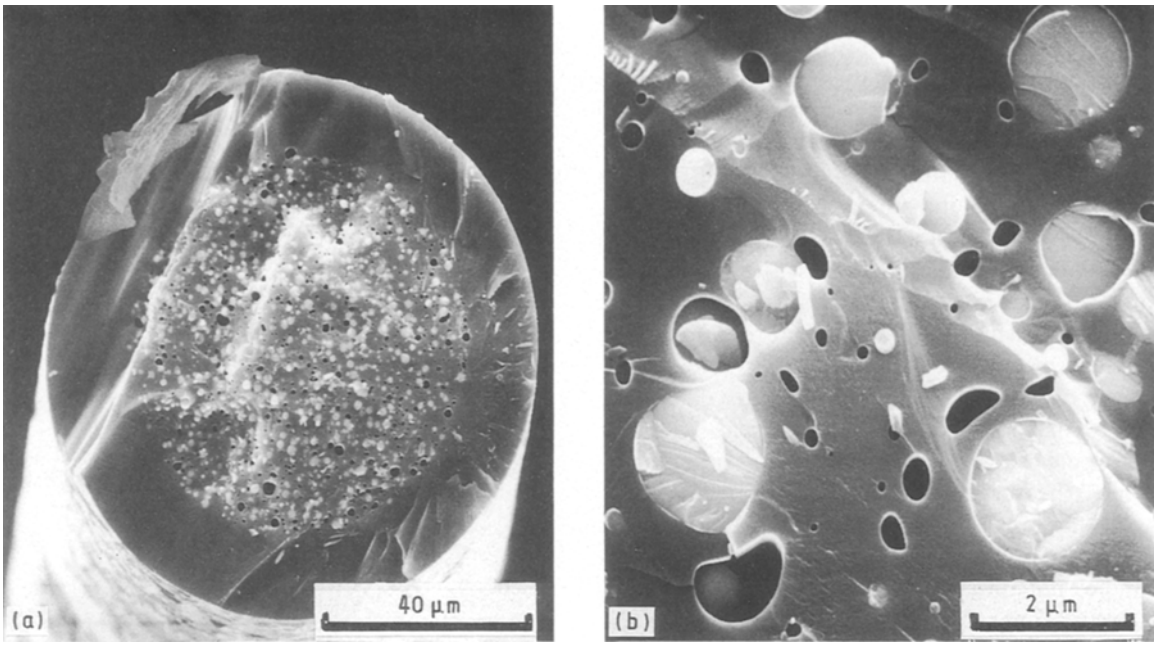

Figure 7 Cross-sectional views of a fibre made by the process illustrated in Fig. 6. Fine germanium filaments in the central portion of the fibre are separated by a porous glass matrix.

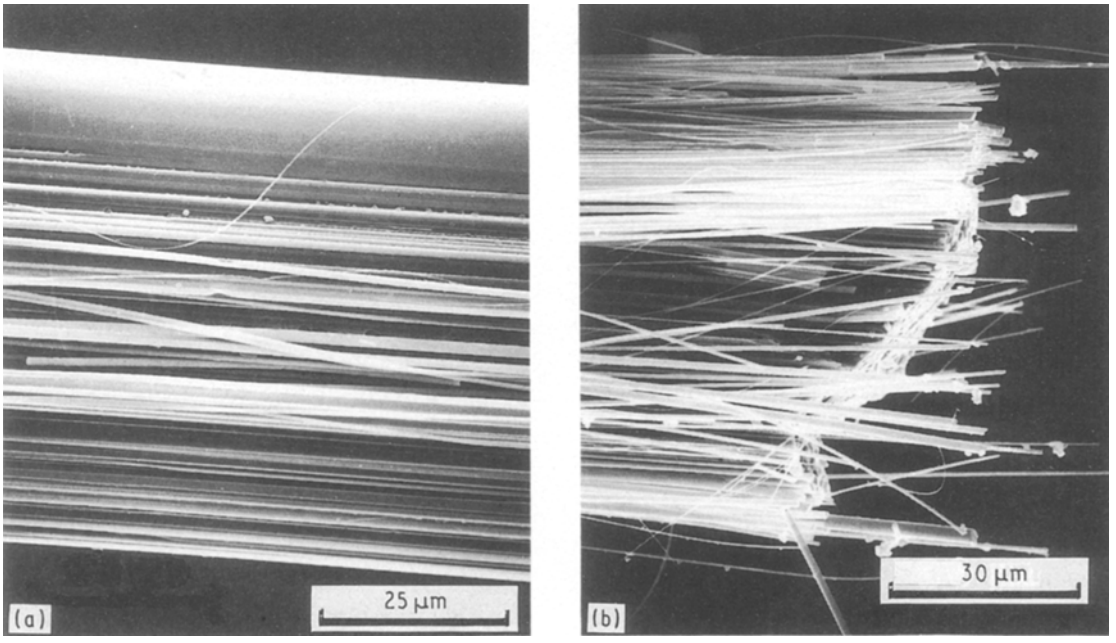

Figure 8 Longitudinal views of the fibre in Fig. 7 after it was etched to remove part of the glass. (a) A region where part of the glass sheath remains, (b) a cut end where only a small central region still contains glass.

over long distances. Electrical resistivity measurements made on filaments extracted from this fibre showed that their resistivity had decreased from the 40 Ω cm value of the unprocessed germanium to about 1 Ω cm, but the filament still exhibited semiconducting properties [10].

Fibres made with metal powders, such as with copper, had much shorter filament lengths than those seen with germanium. These effects and other fibre characteristics are discussed in Section 3.3.

3. Discussion

The processes discussed above have some features in common with one another and some which are quite different. Two of the common features will be considered first, and then their unique features will be considered.

One feature common to the different process variations described above is that they are all simple to execute. With all three variations, fibre can be drawn so long as the glass is fed into the hot zone if the feed rate, pulling speed, and heater temperature are maintained at approximately constant values. This simplicity results from the manner in which core materials are introduced into the glass tubes or capillaries; that is, by filling the glass with a powder or, in the repeated drawing variant, by placing a single Taylor wire within it. The use of such simple charging methods is not

original, but we believe that the use of an applied vacuum to promote uniform collapse of the glass is. None of the processing methods described above work well if the glass is not evacuated. With the powder-fill processes, gases in unevacuated tubes will expand on heating and produce gross voids. Gases are trapped to a lesser degree when an air-filled capillary charged with a Taylor wire is drawn into a fibre, but the fibre does contain pores, and these pores can relax the constraints on the inner filament to such an extent that spheration occurs as the glass is heated. These problems are eliminated by using only a simple mechanical vacuum pump. No efforts have been made to monitor pressures.

Problems associated with the volume change during solidification are common to all three processes. The method described by Taylor in his 1931 patent [6], of quenching the fibre with water just beyond the hot zone of the fibre-drawing apparatus, has been applied with some success to the pulling of simple Taylor wires, but it has not proven to be beneficial when employed with the multiple-drawing process or the multifilament process. Our lack of success with these processes is, we believe, in large measure attributable to the fact that we have not succeeded in quenching the fibre close enough to the melt reservoirs in the heated tubes or capillaries. It is relatively easy to effect the necessary flow of fluid between the reservoir and the solid/liquid interface when the filament is coarse, but it becomes progressively more difficult as the filament diameters are reduced, as they typically are in the latter two processes. It is known from fluid-flow studies [11] that the pressure needed to maintain constant-velocity laminar flow of a liquid through a capillary varies inversely as the square of the capillary diameter, so the flow distances must be very short when the filament diameters are small. The maintenance of short melt-flow distances, if continuous filaments are to be maintained, imposes the requirement that temperature gradients be steep in the system. The problem of maintaining short melt-flow distances and steep temperature gradients is particularly difficult when filament diameters are large, as they are in the multiple-drawing process and the multifilament process, because the heat must diffuse out through the low thermal conductivity glass fibre. It appears that new heating and cooling methods will be needed if continuity is to be maintained over long lengths of metal filaments with these processes.

3.1. Geometry of Taylor wires

A serious limitation of the processes employed here to produce Taylor wires is that the filament diameters may fluctuate along the length of the fibre. Several factors contribute to the variations, principal among these being that the volume of the fill material drops as the powder melts, and that when the glass collapses to remove the free volume created by the shrinkage, variations occur in the melt-pool diameter. Filament diameter variations observed typically ranged from a few per cent in 10 cm for large diameter filaments to a few per cent per metre in fine filaments. The variation

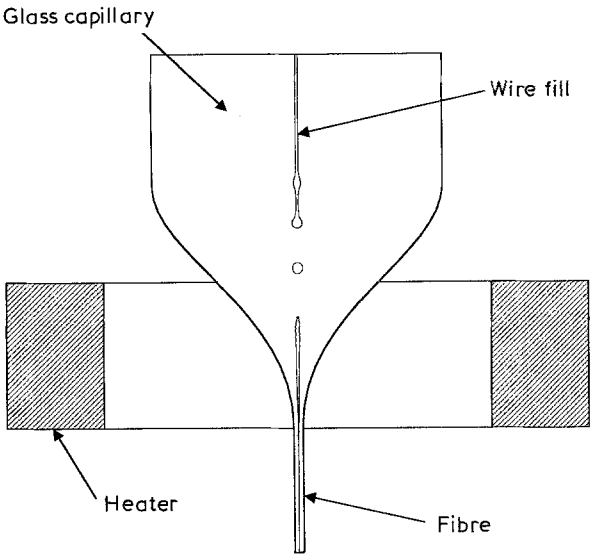

Figure 9 Schematic illustration of fibre drawing from a capillary containing a fine diameter axial wire. The molten wire has broken down into spheres to minimize the glass/melt interfacial area.

in filament diameter was sometimes substantial over long fibre lengths. In fact, the melt column sometimes separated, leaving portions of the fibre without any metal core. While such variations can be minimized by methods, such as those of Parkhachev [4], which maintain a constant melt volume, they did not pose a problem for use in the repeated drawing method for which they were employed in this study. Taylor wires employed in the repeated drawing process were selected so as not to show appreciable variation in filament diameter over the length involved.

Much of the interest in processes related to that of Taylor derives from the fact that they can produce fine metal filaments in a single operation. There appears to have been little systematic study of what factors effect the minimum attainable filament diameter. Taylor [1] apparently believed that submicrometre filaments could be produced from several metals, but the only metal which he presented evidence of having produced in such fine sizes was antimony. Antimony is a convenient metal for him to use because it expands during solidification, making it relatively easy to produce continuous filaments for the resistivity tests he employed and because, with its low liquid/vapour interfacial free energy (0.38 J m^{-2}), it is an easy metal from which to produce fine filaments. Later investigators, working with metals having higher interfacial free energies have apparently not succeeded in producing filaments smaller than 1 μm. Efforts described in Section 2.1 to produce submicrometre filaments in a single-drawing step by employing a small copper wire in a capillary failed, because after melting, the wire broke down into a series of small spheres, as illustrated in Fig. 9. One can appreciate from examination of this figure that when small-diameter metal wires are employed, the melt must persist without breakdown for some time in the softened glass before it advances to the point where it is rapidly reduced in diameter. The melt must also persist in the new reduced diameter until it is cooled to a temperature where breakdown is impossible. Capillaries containing marginally

stable molten metal cores have been removed from the fibre-drawing apparatus, rapidly cooled and examined by optical microscopy for evidence of melt breakdown. No evidence has been seen of initial breakdown occurring after a filament reaches its minimum diameter, but the breakdown sometimes occurs high up in the glass, and it is sometimes observed to occur first in regions where the glass has already been reduced to only a fraction of its initial diameter.

The type of breakdown illustrated in Fig. 9 was not observed when experiments were done with molten cores near 1 mm or more in diameter, but the breakdown into molten droplets observed with finer diameter cores demonstrates that core stability is crucially dependent on core diameter.

3.2. Repeatedly drawn fibres

As described in Section 2.2, the repeated-drawing process, when it employs a high-viscosity inner glass to prevent the interface energy-driven breakdown of the molten filament, makes it possible to produce filaments considerably smaller than the single-step processes. The repeated-drawing process can, in principle, be employed to process a wide range of material types, but its applicability is restricted to some degree by the lack of availability of suitable glasses. The two glasses employed in this study, Pyrex and GE type 180, can be used for the many metals which melt at temperatures below 1100 °C, but there are no compatible glasses available for use with higher melting temperature metals. The only two commercially available glasses with higher working temperatures, Vycor and fused quartz, can be used for single-stage drawing of several metals, but their softening temperatures differ by only about 50 °C, and this is not a great enough difference to provide the high viscosity for the inner glass needed to assure stability of the fine molten-metal core. It would be possible to formulate glasses with working temperatures between those of type 180 and Vycor, but none is available commercially.

A more fundamental shortcoming of the process is that it does not appear possible to produce long filaments of the many normal metals which contract as they solidify. All attempts with multiple drawing of copper and other normal metals have yielded filaments with frequent breaks. As an example, two-stage drawing experiments were done employing Pyrex and GE-type 180 glass fibres containing continuous copper filaments made by slow drawing. The doubly drawn fibres contained filaments about 4 μm in diameter, a diameter which is large compared to the fine filaments discussed earlier. Examination of the fibres confirmed that the filaments had many breaks, with the continuous sections having an average length of 1.4 mm, and with the minimum and maximum lengths being 0.1 and 6.8 mm. The length to diameter ratio of the copper filament segments were thus of the order of 10^3 compared to values as high as 3×10^5 with bismuth filaments.

The breaks observed between filament segments in the copper-containing fibres varied between about 4 and 364 μm, and had a mean length of 52 μm. The ratio of mean gap length to mean filament length was 0.037, which is near the value expected for the volume change upon solidification. This is as it should be, because with this materials combination, the melting point of the metal is near the drawing temperature, so that the difference in expansion coefficients is not as important as it is with bismuth. It is apparent from these observations that if the bismuth were drawn in a glass with a lower working temperature or with a greater expansion coefficient it might be possible to make filaments which were truly fine and continuous over great lengths. The same should be true of antimony, GaSb, InSb and some other compounds which expand on freezing.

It is possible that with the multiple-drawing process, as with single-stage Taylor processes, effective quenching of the copper-containing fibre could permit feeding of melt to the solidification interface and prevent the formation of gaps, but attempts to do this have, to date, been unsuccessful. This approach is more difficult with multiply-drawn fibres than with typical variations of the Taylor process because the relatively thick glass sheaths of multiply-drawn fibres make it difficult to establish the steep temperature gradients necessary to permit flow of melt to the solidification interface. The problem becomes rapidly more difficult as the core diameter is reduced because of the flow problem mentioned early in the discussion. The dependence of the flow rate on the inverse square of the filament radius makes it unlikely that the repeated-drawing method could be used to produce long, continuous filaments of normal metals with filament diameters substantially less than 1 μm diameter.

3.3. Multifilament fibres

The photographs shown in Figs 7 and 8 demonstrate that the multifilament process is capable of producing fibres with a great many parallel filaments. Under ideal conditions, each metal powder particle in the initial blend of metal and glass powders will be drawn out into a filament. Conditions are generally not ideal, but, before considering those situations where interactions occur between powder particles, the response of isolated powder particles will be described.

For the experiments reported here, the glass particles, produced by crushing tubing of the appropriate glass, are of very irregular shape and hence the metal (or germanium) particles are surrounded by loosely packed glass shards. When the tube containing the powder aggregate advances into the hot zone, as represented in Fig. 6, the glass is consolidated into a viscous, somewhat porous mass, and the metal-powder particles melt. Observation of the process with a low-power optical microscope revealed that the individual droplets persist in a nearly spherical shape until the tube is advanced to a position where drawing of the fibre causes a rapid reduction of the tube diameter. It is apparently only at this relatively late stage in the process that the glass can apply enough force to the metal droplet to cause it to begin elongating into a

filament. The diameter reduction experienced by the droplet is thus less than that experienced by the tube. The fibre pictured in Fig. 7 is 96 μm in diameter, and it was drawn from a 10 mm diameter tube, so the gross reduction ratio was approximately 100 : 1. The maximum germanium particle size charged into the tube was 63 μm and the maximum filament diameter is just under 2 μm, so the diameter reduction ratio of the droplets was approximately 30 : 1. These ratios suggest that the droplets did not begin to be reduced to filaments until the tube was reduced to about one-third its initial diameter, in accord with the microscopic observations.

If a 63 μm diameter droplet were reduced by a uniform drawing ratio to a filament with a maximum diameter of 2 μm, the resulting filament would be about 57 mm long. Because the initial crushed germanium particles were of irregular shapes, some of the droplets would be more than 63 μm diameter, so a few of the filaments contained within the fibre pictured in Figs 7 and 8 might be expected to have somewhat longer filament lengths. At least some of the filaments must be considerably longer than 57 mm, however, as was demonstrated by electrical resistance measurements. Electrical contact with the filaments within a length of fibre was established by wetting short lengths of the fibre with eutectic Ga–In alloy (which is molten at room temperature) and then cutting the fibre with a razor blade within the melt pools. Resistance measurements with a high-impedance multimeter showed that electrical continuity was maintained over fibre lengths as great as 720 mm. The resistance did not vary uniformly with the length of fibre examined, as is demonstrated in Fig. 10. The variation of resistance with length was even greater than suggested by Fig. 10 because several of the fibre segments examined showed resistances beyond the 20 MΩ range of the multimeter. These resistance measurements demonstrate that some continuous conduction paths persist over distances which are far greater than those which could result from the drawing out of a single 63 μm droplet into a discrete filament.

There are at least two mechanisms by which longer conduction paths could have been established during the fibre drawing. One of the possible mechanisms is known to occur with germanium powder when the processing temperature is 30–50 °C higher than that used to draw the fibre pictured in Figs 7 and 8. This mechanism consists of many small melt droplets agglomerating into a large droplet which is then drawn out into a relatively coarse filament. Observations of the processing with a low-power optical microscope under conditions which yielded these larger filaments revealed that many of the individual germanium droplets were joining into larger droplets in the region where the diameter of the glass tube was being rapidly reduced. These large droplets were then drawn out into relatively coarse filaments which would be longer than those formed from small isolated droplets. It is believed that the agglomeration of particles occurred because the glass was heated to a temperature where its viscosity was sufficiently low that the weight of the droplets caused them to sag down

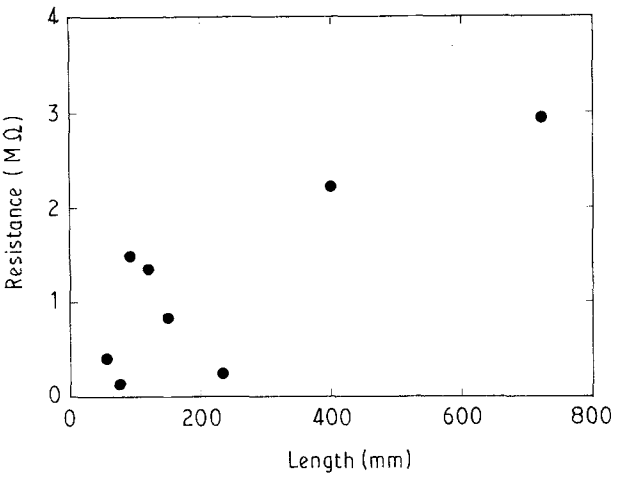

Figure 10 Electrical resistance of multifilamentary germanium containing fibre segments of different lengths.

through the porous glass matrix. Under such circumstances the larger droplets would move fastest and would sweep up small droplets in their path. Because the germanium particles had initial separations of only a few hundredths of a millimetre, little motion would be required to produce quite large particles. When these large droplets were drawn out into filaments, some of the filaments had diameters of 5 μm or more. No effort has been made to measure the length of these relatively large diameter filaments, but it can be estimated using the conservation of matter calculations employed above. If a filament with a maximum diameter of 5 μm were formed from a single droplet by a uniform 30 : 1 diameter reduction, the starting diameter would have been about 150 μm. A uniform 30 : 1 diameter reduction of such a droplet would yield a filament 135 mm long. Such filaments could not account for the resistances measured on germanium-containing fibres. Filaments of even greater diameter were seen in poorly processed fibres, but the fibres which were studied had few, if any, filaments larger than 3 μm diameter. Some other mechanism, such as that outlined in the next paragraph, must account for the observed resistance results.

Just as the original small molten droplets can join into larger droplets when the drawing temperature is excessive, it seems likely that the compressive stresses exerted on the small molten droplets during drawing will sometimes cause a portion of the droplet to be extruded into the pores remaining in the glass matrix, causing a protrusion to form on the filament. Such protrusions might also form when the expansion during solidification causes a small amount of the melt to squeeze out into a neighbouring pore. These protrusions should occasionally make contact with neighbouring filaments, creating electrical paths which are longer than the individual filament lengths. Such contacts between discrete filaments have not been observed, but examination of the fibres in cross-sectional views such as that in Fig. 7, show that some filaments do have bumps on them. Contacts formed in the manner just described would occur in a very irregular fashion, so the number of long conduction paths should vary substantially from one portion of the fibre

to another, as one would surmise from the resistance results.

The multifilament process has been used to make fibres containing a number of different metals and alloys. Because of their shrinkage during solidification, the metals invariably have shorter filament lengths than does germanium. Some of the fibres also exhibit porosity of the sort discussed above. Porosity was a particular problem when attempts were made to draw multifilamentary fibres using copper powder in Pyrex glass. Copper melts nearly 150 °C higher than germanium (1083 versus 937 °C), and, when the glass was heated to a temperature hot enough to melt the copper powder, the fibres showed marked porosity and only a few coarse filaments. The porosity apparently resulted from outgassing of the Pyrex powder. Many glasses outgas when they are heated, but bulk Pyrex normally does not show evidence of doing so at such low temperatures. Repeating the experiment with type 180 glass tubing containing a mixture of copper powder and crushed 180 glass yielded better results. When heated to a temperature sufficient to draw fibres containing copper filaments, the 180 glass shows no sign of outgassing, and the fibres show a degree of porosity comparable to that evident in Fig. 7. The copper filaments were, however, broken into segments which were normally less than a millimetre long.

Multifilamentary fibres have also been drawn using an oxygen–hydrogen torch and the glass lathe apparatus described in Section 2.1. This processing employed several different transition metal alloy powders and either quartz glass or Vycor. Alloys processed include several permalloy compositions (i.e. composition near Ni–20% Fe), several sendust alloys (soft magnetic alloys based on Fe–Si) and a few glass-forming alloys based on iron, nickel or cobalt with boron and silicon to promote glass formation. Processing was done on a trial and error basis because no method was available to measure the glass temperature, but suitable conditions were found for all alloys. The fibres had fewer filaments than is pictured in Figs 7 and 8, but many of the filaments had diameters near 1 μm. This drawing apparatus was equipped with a water-quenching device which could be positioned very near the drawing zone. Quenching with this device was found to be effective in producing long lengths of continuous monofilaments from powder-filled capillaries, but it was not effective in producing continuous filaments in the multifilamentary fibres. This failure is believed to have been due to the fact that the multifilamentary fibres produced in this way were relatively coarse (about 100 μm diameter), so that the rate of heat removal was insufficient to keep the solidification interface in the individual filaments near enough to fatter portions of the molten-metal droplet to permit melt flow to the interface. This is not a surprising result because the difference in melting temperatures between the alloys studied (about 1100–1450 °C) and the drawing temperature of the glass (something over 1800 °C) is so great. Visual observations of the optical radiation from the metal within the fibres suggested that solidification was probably complete by the time the fibre had been submerged in water for a distance of about 1 cm. The glass would have cooled to below its softening temperature in a fraction of that distance, so the solidification interfaces were probably several millimetres from the unreduced droplets. It would be surprising if melt flow were possible over such distances in capillaries near 1 μm diameter.

4. Conclusions

The new processing methods described make possible the drawing of glass fibres containing single conducting filaments with diameters substantially finer than a micrometre and of fibres containing many parallel filaments with micrometre-scale diameters.

Filaments produced by both processes are generally broken into segments a few millimetres long, though in some instances the filaments are much longer.

Repeated drawing of fibres containing bismuth produced filaments as small as 20 nm diameter. Filaments only 42 nm diameter were observed to be continuous over lengths as great as 15 mm.

The multifilament process has been successfully employed with metals having melting points as high as 1450 °C, but the requirement for two glasses with appropriate differences in their softening temperatures appears to limit the use of the multiple-drawing process to metals with melting temperatures below about 1100 °C.

Acknowledgements

The author is indebted to W. P. Robey and E. S. Hartman for invaluable help with the fibre drawing and to K. P. Cooper and Harry Jones for their generous help with electron and optical microscopy. Financial support from the Office of Naval Research is gratefully acknowledged.

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Received 12 December 1991
and accepted 2 September 1992