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Review
Production, properties and applications of microwire and related products

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Methods available for the production of microwire, defined as fine filament of circular cross-section and diameter less than 100 μm, are reviewed, with particular attention being devoted to the versatile Taylor-wire route. The process parameters which are considered to be important in determining the quality of material produced by this and other related techniques, and the types and properties of microwire, are outlined and compared. Techniques for producing related materials, including fibre of non-circular cross-section and narrow ribbon, are also reviewed briefly. In conclusion, a number of potential applications for microwire materials are discussed.

1. Introduction

Microwire, defined in this review as continuous metallic filament of diameter less than ~100 μm and of circular cross-section, has applications or potential applications in a number of areas, including miniature electrical or electronic components, screens and filters, and composite materials. Conventional methods for producing microwire rely on mechanical drawing of solid feedstock to the required dimensions. Drawing through dies becomes less practical, however, as the required diameter decreases below about 50 μm. Hence, although in principle ductile metals can be drawn down mechanically to diameters of the order of 5 to 10 μm, the process requires repeated drawing and annealing stages, and is therefore labour-intensive and expensive. Methods which rely on producing microwire in one operation directly from the melt, on the other hand, are intrinsically inexpensive, and have been used successfully to produce a wide variety of metals and alloys in sizes ranging from more than 100 μm diameter down to ~1 μm.

The methods available for producing fine microwires directly from the melt, from the pioneering work of Taylor in the 1920s [1] to the present day, are outlined in this review. Particular attention is given to the types of material that have been produced in various laboratories around the world, and to those process parameters which are considered to be important for the production of high-quality material. Alternative methods for producing microwire materials from the solid state are also reviewed. In addition, some techniques for producing related products, including fibres of non-circular cross-section and narrow ribbon, are summarized; and, finally, possible applications of microwire and related materials are presented.

2. Methods for producing microwire

2.1. The Taylor-wire process

2.1.1. Description of the original method

A process for producing fine metal wires directly from the melt was first reported by Taylor [1] in 1924. Further details of the basic technique, which is illustrated schematically in Fig. 1, were subsequently patented in 1931 [2]. In the original method, which became known as the "Taylor-wire process", the metal to be drawn was contained in a glass tube ~2 mm internal diameter, which was closed at one end. This end of the tube was heated in a gas flame until the metal melted and the glass softened, when the tube was drawn down, by hand, to produce metal-filled rods ~0.5 to 1.0 mm diameter by about 300 mm long. Subsequently, these rods were re-drawn to the diameter required by passing through a heated metal cylinder held at a temperature appropriate for the metal in question, the metal cylinder providing a uniform temperature zone which aided in producing a continuous filament of high quality. A cooling device, consisting of a water-cooled metal cylinder situated immediately after the heating zone, was also noted to be highly beneficial as an aid for producing continuous filament.

Taylor claimed to have produced a variety of metals in the form of fine glass-encapsulated filaments of diameter down to below 1 μm by this method, including iron, copper, silver, gold, cadmium, aluminium, gallium, indium, thallium, tin, lead, antimony and bismuth. He emphasized that the glass used in the operation must be compatible with the metal in question, i.e. there should be no chemical reaction at the drawing temperature, and the softening or working point of the glass must fall between the melting and boiling points of the metal concerned. Fused silica

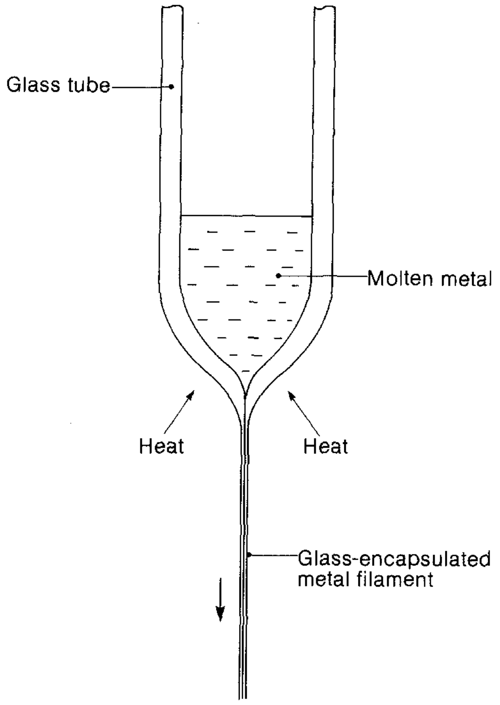

Figure 1 Basic Taylor-wire principle.

was apparently used successfully for preparing filaments from iron, copper, silver and gold, whereas softer glasses were used with other lower melting point metals. Due to its reactivity with silica, aluminium required the use of a silica-free sodium borate glass. Taylor noted that, if required, the glass coating could be removed using aqueous HF solution, although for many potential applications, particularly in the electrical industries, an insulating glass coating could be an advantage.

2.1.2. Later developments

Little interest was initially shown in this novel process for producing microwire, probably because viable large-scale commercial applications for fine metal filaments were severely limited at that time, and the materials were mainly regarded as laboratory curiosities. By the 1950s and 1960s, however, significant attention was being shown in the Taylor-wire process particularly by workers in the USSR [3–8], with more limited interest exhibited by researchers in the USA [9–11], the UK [12–14] and Europe [15–18], driven mainly by the potential applications of microwire in the miniature electrical components industries.

Since the early 1970s interest in the Taylor-wire process has apparently declined somewhat in the Soviet Union [19, 20]. In Europe [21–26], the US [27] and the UK [28] reported interest has continued at a relatively low level. In Japan, however, a considerable degree of effort has been devoted to this route for producing microwire materials, particularly over the last ten years [29–49]. A great revival in microwire topics has thus been initiated recently, due mainly to the work of Gotō and co-workers [29–49] at the Nagoya Institute of Technology and the present time is therefore ideal for a review of this nature.

Many different types of metal and alloy have now been successfully prepared in microwire form by the Taylor-wire route, with core diameters ranging from ~ 1 μm to more than 100 μm, and glass coating thicknesses of the order of 2 to 30 μm. The developments that have taken place since the pioneering work of Taylor [1, 2] are outlined in the following sections, and some of the data are summarized in Table I.

2.1.2.1. Developments in the USSR. Interest in the commercial production of microwire in the USSR was reported by Ulitovsky [3] in 1957. He claimed that glass-coated metal microwires with core diameters in the range 2 to 20 μm had been produced successfully in the USSR in the period since 1949. Various materials including copper, iron and manganin (86 wt % Cu–12 wt % Mn–2 wt % Ni alloy) were being produced as microwire at that time on a commercial scale with, it was claimed, applications in the electrical industry as resistors, coils for galvanometers and related devices. Details of the process employed in the production of the microwires were later disclosed in a number of patents [4–8], from which it was clear that a modified Taylor-wire process was being used which enabled semi-continuous production on a commercial scale of relatively uniform materials.

In one report, Baikov [4] specified that the method involved feeding a glass tube, closed at one end and containing a metal pellet and feed-wire, continuously into an h.f. inductively heated zone at a predetermined rate which could be varied. The metal within this zone melted and caused the glass tube to soften in this region. Drawing was then initiated, and the resulting metal-cored glass fibre wound on to a take-up drum driven by an electric motor. It was claimed that the diameter of the resulting metal core could be varied by altering the take-up speed of the microwire and the cooling rate, whilst the thickness of glass coating apparently depended mainly on the feed rate of the glass tube into the heating zone, and to a lesser degree on the take-up speed. The process is shown schematically in Fig. 2. The cooling rate, which governs the solidification time, could be increased, it was claimed, by incorporating an air or liquid jet, through which the microwire must pass, just below the induction coil.

In subsequent patents [5–8] details of further refinements to the process were given. These were aimed mainly at more efficient commercial operation, for production of reproducible materials on a semi-automatic basis. It was reported [7, 8], for example, that close control over dimensional tolerances and electrical resistivity of the microwire could be achieved by monitoring continuously the electrical resistance of the microwire as it was produced, by an impedance method. If, during production, the resistivity varied outside pre-set limits, automatic adjustment of the process conditions could be initiated by the incorporation of suitable feedback circuitry. Some details of suitable glasses employed in the production of a number of microwire materials were also discussed [5, 6]; details are summarized in Table II. It was emphasized that both the glass and metal feedstock employed in the production of microwire should ideally be thoroughly cleaned, degreased and vacuum-annealed prior to use, in order to obtain a high-quality continuous product. Failure to adopt this procedure

TABLE I Summary of published data on microwire materials prepared using the Taylor-wire process

Metal core	Core diameter (μm)	Glass employed	Coating thickness (μm)	Drawing temperature (°C)	Drawing speed (m min^{-1})	Reference
Crystalline materials						
Cu, Ag or Au	Down to $\sim 1\ \mu$m	Fused silica or borosilicate	–	–	–	[1, 2]
Fe		Fused silica	–	–	–	
Al		Sodium borate	–	–	–	
Pb, Sn or Bi		Most common glasses	–	–	–	
Tl		Borosilicate	–	–	–	
Cd or Ga		Common soft glasses	–	–	–	
Sb		Sodium borosilicate	–	–	–	
Cu, Fe or manganin alloy	1 to 50	See Table II	5 to 10	1300	–	[3–8]
Cu	38	Pyrex borosilicate	19	–	90	[9]
316 stainless steel	127	Vycor fused silica	–	–	–	
Cu, Cr, Fe, Al, Be or Sn	–	Fused silica or Pyrex borosilicate	–	1600 to 2080	–	[10]
Cu	1 to 20	Pyrex borosilicate	15 to 30	1300	–	[12, 13]
Fe–B–Sn alloy		Pyrex borosilicate				
Ni–Si alloy		Pyrex borosilicate				
Ni–Cr–Sn alloy		Pyrex borosilicate				
Ni–Cu–Bi alloy		Pyrex borosilicate				
Fe, stainless steel and maraging steel	2 to 100	Fused silica	–	–	10 to 1000	[15–18]
Ag or Au	5 to 40	Pyrex borosilicate	5 to 30	1300	–	[21, 23]
Cu	10 to 50	Supremax borosilicate	5 to 30	1300	–	
Cu	2 to 50	–	–	–	–	[25]
Ag	30	–	–	–	–	
Au	50	–	–	–	–	
Fe, Co, Te	50	–	–	–	–	
Pb	10	–	–	–	–	
Fe–P, Fe–As and Pb–Bi alloys	5 to 30	–	–	–	–	
Cu–Si alloy	2 to 7	–	–	–	–	
Alloys of Ge with Fe, Co, Ni, Ag and Au	15	–	–	–	–	
Cu	2 to 12	Pyrex borosilicate	–	1300	60 to 480	[31, 32]
Fe	4 to 53	Vycor fused silica	–	2000	60 to 480	[31, 32]
Ag	2 to 13	Pyrex borosilicate	–	1200 to 1250	60 to 480	[33]
Au	3 to 13	Pyrex borosilicate	–	1200	60 to 480	[30, 36]
Cu–Ag alloy	3 to 9	Pyrex borosilicate	–	1300	160 to 480	[37]
Ag–Cu alloy		Pyrex borosilicate	–	1300	160 to 480	[37]
Fe–B alloy	–	–	–	–	–	[38]
Fe–Si–B alloy	–	–	–	–	–	
Fe–Ni–B alloy	–	–	–	–	–	
Fe–Co–B alloy	–	–	–	–	–	
Fe–Cr–B alloy	–	–	–	–	–	
Ni–Cr–Mo–Fe alloy (Hastelloy X)	3 to 5	Pyrex borosilicate	–	1360	60 to 240	[39]
V_3Si	> 50	Vycor fused silica	–	> 1995	–	[40]
Cu–Si–V alloy	6 to 12	Pyrex borosilicate	–	1360	90 to 480	
Cu–Ge–Nb alloy	9 to 11	Pyrex borosilicate	–	1360	90 to 480	
Cu–Sn–Nb alloy	6 to 16	Pyrex borosilicate	–	1360	90 to 480	
Cu–Nb–Si alloy	–	–	–	–	–	[42]
Cu–V–Si alloy	6 to 10	Pyrex borosilicate	–	1325	60 to 235	[41]
Cu–V–Si alloy	> 50	Vycor fused silica	–	–	–	[41]
Ni–B alloy	4 to 12	Pyrex borosilicate	–	1325	60 to 480	[43]
Ni–Si–B alloy	4 to 15		–			
Ni–Fe–B alloy	5 to 14		–			
Ni–Fe–Si–B alloy	5 to 15		–			
Ni–P–B alloy	5 to 16		–			
Ni–P–Si alloy	6 to 20		–			
Ni–Fe–P–B alloy	5 to 21		–			

TABLE I Continued

Metal core	Core diameter (μm)	Glass employed	Coating thickness (μm)	Drawing temperature (°C)	Drawing speed (m min^{-1})	Reference
Pb	13 to 26	Pyrex borosilicate	–	1175	60 to 480	[44]
Pb–In alloy	21 to 78		–		60 to 160	
Pb–Sn alloy	8 to 39		–		60 to 160	
Pb–Au alloy	32 to 58		–		60 to 160	
Pb–Bi alloy	15 to 67		–		60 to 480	
Fe–C–B–Mn alloy	1 to 15	–	3 to 7	–	–	[20]
Pb–In–Bi alloy	53 to 84	Pyrex borosilicate	–	1225	60 to 480	[45]
Pb–Sn–Bi alloy						
Pb–Sn–Ge alloy	11 to 38	Pyrex borosilicate	–	1225	160	[46]
Pb–Bi–Ge alloy	13 to 71	Pyrex borosilicate	–	1225	60 to 240	[47]
Fe–Ni–Cr–Cu–B–Si alloy	3 to 18	Pyrex borosilicate	–	1325	60 to 480	[48]
Fe–Co–Cr–Ni–Cu–B alloy	4 to 14	Pyrex borosilicate	–	1325	60 to 480	[49]
Fe–Co–Cr–Ni–Cu–B–Ti alloy		Pyrex borosilicate	–	1325	60 to 480	
Amorphous materials						
$Fe_{83-x}P_{17}M_x$ (M = Ga, Ge or As, x = 2 to 8 at %)	10 to 20	Fused silica	–	–	120	[24]
$Fe_{80}P_{16}C_3B_1$	5	Pyrex borosilicate	–	1200	480	[34]
$Fe_{76}C_{15.5}Si_{2.5}Mn_{1.7}B_{4.3}$	1 to 3	–	–	–	–	[19]
$Fe_{80}B_{20}$	–	Pyrex borosilicate	–	–	> 240	[38]
$Fe_{76.5}Si_{8.5}B_{15}$	–		–	–	> 240	
$Fe_{68}Si_{17}B_{15}$	–		–	–	–	
$Fe_{80}C_{20}$	2	–	4	–	–	[20]
$Ni_{20}Fe_{60}B_{20}$	5 to 7	Pyrex borosilicate	–	1325	> 240	[43]
$Ni_{25}Fe_{50}Si_{10}B_{15}$	6 to 12		–		> 60	
$Ni_{80}P_{20}$	4 to 6		–		> 240	
$Fe_{80}P_{20}$	7 to 19		–		> 60	
$Ni_{60}Fe_{20}P_{20}$	6 to 15		–		> 240	
$Ni_{60}Fe_{20}P_{16}B_4$	5 to 7		–		> 240	
$Ni_{20}Fe_{60}P_{16}B_4$	5 to 14		–		> 60	
$Ni_{75}Fe_{15}Si_{10}$	6		–		> 240	
$Ni_{50}Fe_{25}P_{15}Si_{10}$	8 to 16		–		> 60	
$Ni_{25}Fe_{50}P_{15}Si_{10}$	5 to 14		–		> 60	

could result in gaseous reaction products forming at the glass–metal interface, leading to filament rupture, or to material of low and variable quality.

More recently, Miroshnichenko *et al.* [19] have reported the results of some property measurements that they have made on Fe–C–B–(Mn–Si) alloys prepared by the Taylor-wire route, whilst Bashev [20] has reported some results for Fe–C and Fe–C–Si microwires.

It was possible, until a few years ago, to obtain samples of commercially produced microwire materials from the USSR, but production for external distribution has now apparently ceased.

2.1.2.2. Developments in the United States. After the initial work by Taylor [1, 2], only limited interest has been shown in the microwire process in the United States. One report by McKenica [9] gave details of a modified and updated Taylor-wire method in 1965. The basic modifications were similar to those reported by Baikov [4], and the technique employed a glass tube containing metal feedstock in the form of a thin rod

TABLE II Compositions of glasses used in microwire preparation, after Zaborovsky *et al.* [6]

Glass grade	Electrical resistance of glass ($10^3\,\Omega\,m^{-1}$)	Viscosity of glass at 1300° C (10^3 poise)*	Glass composition (wt %)							
			Na_2O	K_2O	B_2O_3	PbO	Al_2O_3	CaO	Fe_2O_3	SiO_2
Low resistance	< 10	1.8	2.0	2.0	16.0	5.0	< 2.0	< 1.0	< 0.2	75.0
Medium resistance	10 to 20	1.5	2.7	1.2 to 1.8	16.0	5.5	< 1.8	< 1.0	< 0.2	72.0
High resistance	> 20	1.1	3.0	2.0	18.0	5.0	< 2.0	< 1.0	< 0.2	72.0

*1 poise = $10^{-1}\,N\,sec\,m^{-2}$.

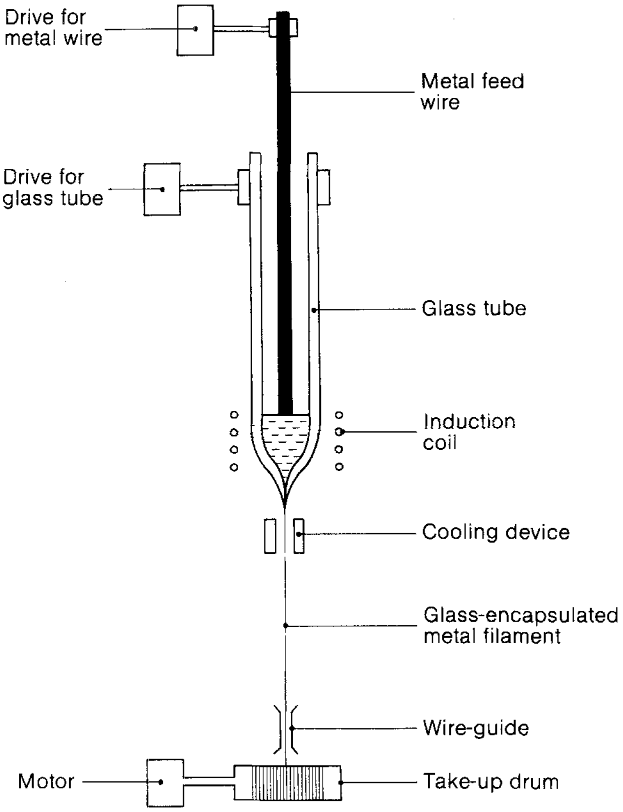

Figure 2 Details of a typical Taylor-wire machine for production of continuous filament.

heated inductively. The induction coil consisted of a conical helix; this was presumably to aid in maintaining melt stability and in achieving levitation of the melt pool within the glass tube, so as to minimize the possibility of the melt breaking through the bottom of the tube under its own weight. It was claimed that the method was particularly suited for producing microwire from beryllium, aluminium, chromium, iron, nickel, copper, silver, gold and alloys of these, using Pyrex borosilicate or fused silica glasses. Specific examples were given for the production of copper and stainless steel wires. The diameter of the resultant metal core was reported to be dependent on the initial diameter of the glass tube, the take-up rate, the feed-in rate of the glass and metal feedstock into the heating zone, and the overall temperature. It was noted that if the temperature was too high, giving too low a glass melt viscosity, fibre drawing was very irregular, whilst if the temperature was too low, resulting in too high a glass viscosity, a discontinuous metal core was obtained.

Cox *et al.* [10] have also given details of the preparation of microwires from a variety of metals, including beryllium, aluminium, chromium, iron, copper and tin, using the Taylor-wire principle. They noted that beryllium was particularly difficult to fabricate by this method, due to the extreme reactivity of molten beryllium with most oxide glasses. Several methods were adopted in an attempt to limit the contact time of the molten metal with the glass, but only minor success was achieved; consequently, continuous lengths of beryllium microwire could not be produced. It was noted that glass coatings could be removed from microwire, if required, by dissolution in molten sodium carbonate.

Some work on property evaluation of copper microwires has also been reported by Soltis [11], and Pond *et al.* [27] have summarized various methods used at Battelle Columbus for producing microwire and related materials, including the Taylor-wire process.

2.1.2.3. Developments in the United Kingdom. A significant degree of interest was also shown in microwire materials produced by the Taylor-wire process by Glass Developments Ltd in the UK in the 1960s [12–14]. Much of the work was carried out using copper drawn in Pyrex borosilicate glass, and samples were then available from Glass Developments with a range of core sizes. Some work was also carried out on other higher melting point metals and alloys, including iron, nickel and various alloy steels, with limited success [12]. It was emphasized that there was a lack of commercially available glasses suitable for drawing metals and alloys which have melting points of around 1400 to 1550° C. For example, Pyrex borosilicate glass has too low a viscosity in this range to enable successful drawing of continuous filaments, whilst fused silica cannot be drawn reliably and consistently below about 2000° C, a temperature at which significant reaction occurs with most metals.

These difficulties were partly overcome by the addition of alloying constituents to the metal which lowered the liquidus and solidus temperatures, and lowered the surface tension. In this way, iron microwires could be drawn successfully into continuous filament of high quality using Pyrex borosilicate glass by alloying the metal with 4 wt % B + 2 wt % Sn. Similarly, nickel filament was produced by alloying with 30 wt % Si, whilst Ni–Cr and Ni–Cu resistance alloys were prepared in microwire form by alloying with tin or bismuth.

Development of microwire materials subsequently ceased at Glass Developments [14], due mainly to a lack of large-scale commercial applications for microwire at that time.

More recently, Pardoe *et al.* [28] have produced microwire-type materials by a method that they describe as the Taylor-wire route. Their method for preparing continuous filament is, however, more closely related to the glass-fibre double bushing technique used for producing graded glass fibres; this utilizes inner and outer bushings which contain the respective molten materials that are to be drawn. They reported the preparation of a variety of materials with different cores which included not only metals, but also oxides, sulphates and halides, with diameters ranging down to $\sim 2\,\mu m$.

2.1.2.4. Developments in Europe. Nixdorf and co-workers [15–18] have published details of work in progress at Battelle Frankfurt in the period up to around 1970. Their modified Taylor-wire process involved feeding a metal rod ~ 2 mm diameter contained in a glass capillary into a heated zone; filament was drawn on to a take-up drum at rates of up to 1000 m min^{-1}, and could be produced in diameters ranging from ~ 2

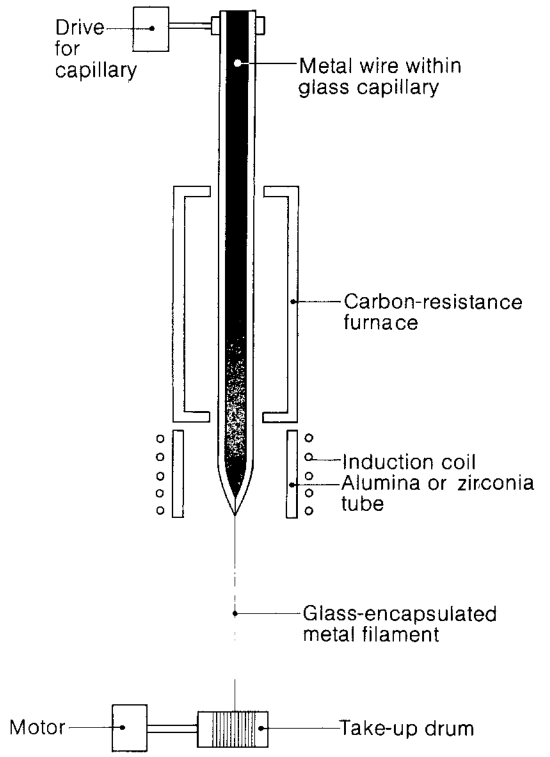

Figure 3 Modified Taylor-wire process for production of refractory metal filaments; after Dannöhl and Nixdorf [16].

to 100 μm. It was claimed that some non-metallic ceramic materials could also be produced in microwire form using this method. It was reported that a number of materials had been successfully produced including iron, stainless and maraging steels, alumina, and the silicides of titanium, vanadium and iron. It was suggested that such materials were ideal for use as reinforcement in composites. The cost of microwire, if produced on a commercial scale of 1 to 10 tonnes per annum, was estimated [18] to be comparatively low, i.e. "several hundred DM per kg" (1970 prices).

If the melting point of the metal is significantly higher than the working range of the glass employed, it would not normally be practicable to produce microwire, because the glass viscosity would be too low and hence the glass would not draw into fibre easily or uniformly. Dannöhl and Nixdorf [16] have, however, patented a modified Taylor-wire process which they claim can be used to prepare glass- or ceramic-coated refractory metal microwires with high melting points. The method, illustrated in Fig. 3, relies on the incorporation of both electrical resistance and inductively heated stages. Feedstock in the form of refractory metal wire in a glass or ceramic tube is preheated first by lowering into a carbon resistance furnace held at a temperature below the softening point of the glass or ceramic concerned. This ensures that the tube and wire reach a uniform temperature before entering the inductively heated zone where, as soon as the metal is molten, fibre is drawn and fed on to a take-up spool, presumably before heat transfer from the metal to the glass reduces the glass viscosity to too low a value. No specific details of materials produced by this method were given. It is unlikely that a crystalline ceramic can be employed successfully as the encapsulating material, because of the poor fibre-drawing characteristics of such materials.

Manfrè and co-workers [21, 23] of Montedison SpA in Italy have reported the production of copper microwires with core diameters in the range 10 to 40 μm. The materials were prepared by a modified Taylor-wire process, similar to that employed by McKenica [9], using a conically wound induction coil. Different borosilicate glasses were investigated and it was noted that the most successful for producing a high quality product was Supremax (manufactured by Schott Glass Works, Mainz, West Germany). The authors emphasized that in order to obtain a product with a continuous metal core, incorporation of a cooling device positioned after the heating zone was essential, its function being to solidify the glass coating before solidification of the metal interior had occurred. It was noted that if the metal became rigid before the glass viscosity had dropped below the working range, further extension of the glass cladding occurred, and this precipitated fracture of the metal core, thereby giving rise to a discontinuous product. The thickness of the glass coating was typically of the order of about half the core diameter; for example, a 5 μm glass coating for a 10 μm diameter core, and a 25 μm coating for a 40 μm wire. The authors presented comprehensive details of the mechanical properties and microstructure of their materials [23], details of which are given in Section 2.1.4.

Other work on Taylor-wire materials includes the preparation of Fe–P–C alloys by Wiesner and Schneider [24], and the preparation of a variety of metal and alloy microwires by Bunge and co-workers [22, 25]. These and other data are summarized in Table I.

Finally, Haour and Bode [26] have summarized a number of methods in use at Battelle Geneva for producing microwire-type materials, including the Taylor-wire method.

2.1.2.5. Developments in Japan. Over the last ten years, up to the present day, Gotō and co-workers of the Nagoya Institute of Technology have published a large number of papers [29–49] dealing with the production of microwire materials by the Taylor-wire process, which they describe as "glass-coated melt-spinning". In their method, a conically wound induction coil is used and metal feedstock in the form of a small ingot ~ 1 g in weight is employed. Further metal additions are not used during a given run. The glass tube is fed into the heating zone automatically at a rate dependent on the drawing speed employed, the take-up speed being varied over the range 60 to 480 m min^{-1}, depending on the diameter of microwire required. Filaments of various metals have been successfully produced, including copper and iron [31, 32], silver [33], gold [30, 36] and lead [44]. In addition, drawing of a number of metallic alloy filaments has been accomplished. This includes materials based on iron [34, 38, 48, 49], nickel [39, 43], copper [37, 40–42], silver [37] and lead [44–47]. Depending on the metal or alloy used, and its precise composition, core sizes in the range 2 to 84 μm have been obtained. A Pyrex

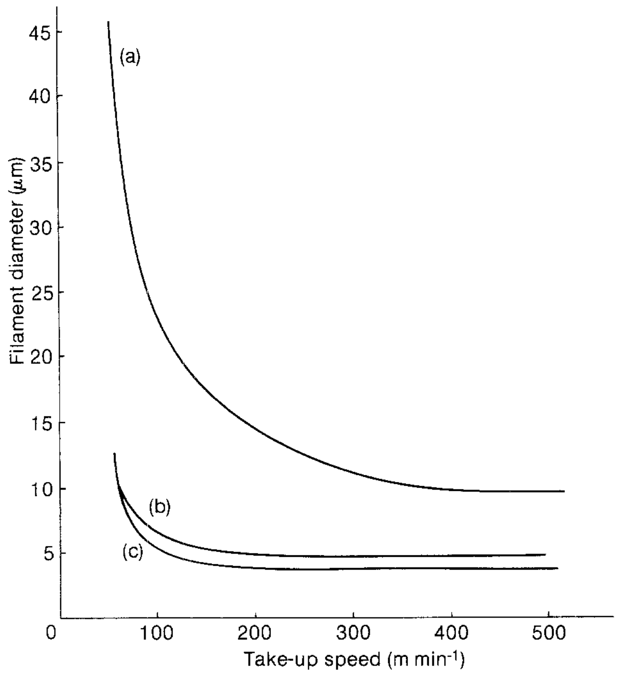

Figure 4 Variation of filament diameter with winding speed for a number of metals; after Gotō and co-workers [31, 36]. (a) Iron drawn in Vycor fused silica; (b) gold drawn in Pyrex borosilicate; (c) copper drawn in Pyrex borosilicate.

borosilicate glass was used for drawing the bulk of the materials at 1200 to 1325° C, whilst Vycor fused silica was found necessary for use with pure iron and for Cu–V–Si alloys containing more than 20 at % V_3Si, at temperatures up to ~2000° C. The data are summarized in Table I.

These authors also have presented comprehensive details of the mechanical properties and microstructures of their materials, details of which are given in Section 2.1.4. In addition, they have provided useful information concerning the systematic approach they took to establish the drawing conditions, in particular the variation of filament diameter with drawing speed, details of which are summarized in Fig. 4.

2.1.2.6. Production of amorphous materials. Depending on the process parameters employed and the diameter of microwire obtained, very high cooling rates, exceeding $10^5\,\mathrm{K\,sec^{-1}}$ for fibre diameters below 10 μm, can be achieved using the Taylor-wire process [15, 19, 35]. Although this is less than can be obtained using some of the more conventional rapid-quenching techniques, for example chill-block melt-spinning at more than $10^6\,\mathrm{K\,sec^{-1}}$, it is still high enough, in principle, to vitrify a number of metallic alloys which have critical cooling rates for glass formation of $\leqslant 10^5$ to $10^6\,\mathrm{K\,sec^{-1}}$.

The first recorded instance of the Taylor-wire process being used successfully to produce amorphous filaments was given by Wiesner and Schneider in 1974 [24]. These authors prepared amorphous $Fe_{83-x}P_{17}M_x$ alloys, where $M = Ga$, Ge or As and $x = 2$ to 8 at %, with diameters in the range 10 to 20 μm, by drawing in fused quartz tubes at a take-up speed of $120\,\mathrm{m\,min^{-1}}$.

Subsequently, reports of further metallic alloys vitrified using the Taylor-wire method were given by Gotō and co-workers. For example, in 1977 Gotō *et al.* [34] reported the successful production of $Fe_{80}P_{16}C_3B_1$ amorphous alloy filaments ~5 μm diameter. Gotō has also prepared amorphous filaments from Fe–B and Fe–Si–B based alloys [38], and also from a number of other iron- and nickel-based alloys [43], ~4 to 12 μm in diameter, by drawing at speeds of normally more than $240\,\mathrm{m\,min^{-1}}$. Mechanical property data have been obtained for these materials, and these are discussed and summarized in Section 2.1.4 and Table III, respectively.

In addition, Miroshnichenko *et al.* [19] and Bashev [20] have prepared amorphous Fe–C–B and Fe–C alloys by the Taylor-wire route.

The critical cooling rate for glass formation for ternary $Fe_{80}P_{13}C_7$ alloy has been estimated [50, 51] to be of the order of $3 \times 10^4\,\mathrm{K\,sec^{-1}}$, whilst that for $Fe_{83}B_{17}$ is $10^6\,\mathrm{K\,sec^{-1}}$. Hence, the estimate for cooling rate by Nixdorf [15] and Gotō [35] of more than $10^5\,\mathrm{K\,sec^{-1}}$ achievable using the Taylor-wire process is in agreement with the experimental data. Many metallic alloys, in addition to the iron- and nickel-based alloys already reported [24, 34, 38, 43], can be vitrified at cooling rates of $\leqslant 10^6\,\mathrm{K\,sec^{-1}}$ [50, 51], including $Co_{75}Si_{15}B_{10}$ ($4 \times 10^5\,\mathrm{K\,sec^{-1}}$), $Fe_{79}Si_{10}B_{11}$ (2×10^5), $Pt_{60}Ni_{15}P_{25}$ (4×10^3), $Pd_{84}Si_{16}$ (3×10^3), $Ni_{60}Nb_{40}$ ($\sim 10^3$) and $Pd_{40}Ni_{40}P_{20}$ ($\sim 10^2$). The Taylor-wire process therefore offers an ideal method for preparing a wide variety of amorphous metallic microwires of circular cross-section. Such materials are far more ideally suited for many property measurements, including mechanical and electrical, than are materials of other geometries produced by more conventional rapid-quenching techniques. One particularly ideal candidate for detailed study employing materials prepared by the Taylor-wire method is the Ni–Si–B ternary system. This system has been systematically and comprehensively investigated by Donald and co-workers [52, 53] using materials produced by chill-block melt-spinning, and it is estimated that many compositions have critical cooling rates for glass formation of much less than $10^6\,\mathrm{K\,sec^{-1}}$.

2.1.3. *Importance of material and process variables in the Taylor-wire operation*

It is clear both intuitively and from the available literature that the successful production of high-quality, continuous filament of given dimensions by the Taylor-wire technique is dependent on a number of critical materials and process factors. These are summarized below.

2.1.3.1. Materials selection.

(a) The glass chosen must be compatible with the metal or alloy at the drawing temperature, i.e. chemical reaction between glass and metal must be negligible.

(b) The glass working (drawing) temperature must be greater than the melting point of the metal or alloy employed, but below its boiling point, or below the temperature at which the metal vapour pressure becomes high enough to disrupt the process.

TABLE III Properties of some microwire materials prepared by the Taylor-wire process

Material	Core diameter (μm)	Crystal phases present	0.2% yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation to failure (%)	Reference
Crystalline materials						
Cu	1	–	–	1625	–	[11]
	1	–	–	2510	–	
	11	–	–	880	–	
	16	–	–	280	–	
	1(o.d. = 35)*	–	–	470 to 520	–	
	5 to 16(o.d. = 35)*	–	–	280 to 560	–	
Cu	10	fcc [100] fibre texture	75 to 170	86 to 180	8.2 to 9.8	[23]
	20		58 to 92	69 to 100	10.2 to 11.2	
	30		70 to 80	75 to 92	12.7 to 13.3	
	40		52 to 65	58 to 70	13.1 to 15.3	
Fe	50	bcc [100] fibre texture	–	–	–	[25]
Co	50	hcp [1231] fibre texture	–	–	–	
Cu	2 to 50	fcc [100] fibre texture	–	–	–	
Au	50	fcc [111] fibre texture	–	–	–	
Pb	10	fcc [100] fibre texture	–	–	–	
Fe–P alloy	5 to 30	bcc + Fe_3P	–	–	–	
Cu	2.5	fcc [100] fibre texture	–	1500 to 2000	2.0	[31]
	10		–	200	15.0	
Au	3.5	fcc [111] + [100] fibre texture	–	290	–	[30, 36]
	5		–	130	7.0	
	7.5		–	70	–	
Fe	4.5	fcc [111] fibre texture	–	2770	1.0	[31]
	10		–	1000	1.0	
	50		–	300	5.0	
Ag	4.7	fcc [100] + [221] or [100] texture	–	370	1.5	[33]
	14		–	100	5.0	
$Fe_{85}B_{15}$	9	bcc + Fe_3B	–	1400	1.8	[38]
	5		–	2400	2.3	
	2		–	3900	2.6	
$Fe_{83}B_{17}$	7	bct	–	1200	1.8	[38]
	4		–	2500	3.7	
$Fe_{80}B_{20}$	7	bcc	–	2100	2.5	[38]
$Fe_{76.5}Cr_{8.5}B_{15}$	–	bct + Fe_3B	–	–	–	[38]
$Fe_{68}Cr_{17}B_{15}$	–	bcc + fct	–	–	–	
$Cu_{86.5}V_{10.1}Si_{3.4}$	7	fct	–	200	1.8	[41]
$Cu_{60}V_{30}Si_{10}$	> 50	fcc	–	130	1.9	
$Cu_{91}V_6Si_2Nb_1$	6	fcc	–	80 to 90	1.5 to 2.2	
$Cu_{85}V_{10}Si_{3.3}Ge_{1.7}$	6	fcc	–	110	3.1	
$Ni_{80}B_{20}$	4	fcc + Ni_3B	–	1500	2.2	[43]
$Ni_{60}Fe_{20}B_{20}$	3	fcc + Ni_3B	–	2000	1.8	
$Ni_{40}Fe_{40}B_{20}$	5	fcc	–	3900	2.7	
$Ni_{75}Si_{10}B_{15}$	4	Double fcc	–	2200	2.2	
$Ni_{75}Si_8B_{17}$	5	fcc	–	3100	2.3	
$Ni_{40}Fe_{25}Si_{10}B_{15}$	7	fcc	–	2900	2.8	
$Ni_{80}P_{16}B_4$	5	Double fcc + Ni_3P	–	1100	1.4	
$Ni_{75}P_{15}Si_{10}$	20	–	–	1400	1.7	
$Pb_{52}Sn_4Ge_{44}$	18	fcc + diamond structure	–	68	1.9	[46]
$Pb_{46}Sn_{22}Ge_{32}$	12	fcc + diamond structure + fct	–	48	0.9	

TABLE III Continued

Material	Core diameter (μm)	Crystal phases present	0.2% yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation to failure (%)	Reference
$Pb_{60}Bi_{15}Ge_{25}$	35	fcc + hcp	–	36	1.3	[47]
$Pb_{39.5}Bi_{42.5}Ge_{18}$	26	fcc + hcp	–	43	0.8	
$Pb_{57}Bi_{30}Ge_{13}$	62	fcc + hcp	–	25	1.4	
$Pb_{71}Bi_{22}Ge_{7}$	71	fcc + hcp	–	24	1.3	
$Fe_{39}Ni_{17}Cr_{30}Cu_{2}B_{6}Si_{6}$	–	bcc	–	3050	3.1	[48]
$Fe_{75}Co_{5}Cr_{5}B_{15}$	12	–	–	2560	2.5	
$Fe_{73}Co_{5}Cr_{5}B_{15}Mo_{2}$	4	–	–	3680	2.5	
$Fe_{73}Co_{5}Cr_{5}Ni_{5}Cu_{2}B_{10}$	13	bcc	–	2040	2.1	
$Fe_{67.5}Co_{5}Cr_{10}Ni_{5}Cu_{2}B_{10}Mo_{0.5}$	3	bcc	–	3180	3.2	
$Fe_{67.5}Co_{5}Cr_{10}Ni_{5}Cu_{2}B_{10}Nb_{0.5}$	5	bcc + fcc	–	2840	3.2	
$Fe_{75.5}Co_{5}Cr_{15}Mn_{10}Cu_{2}B_{10}Ti_{0.5}$	14.5	bcc + fcc	–	1740	11.1	[49]
$Fe_{68}Co_{5}Cr_{10}Ni_{5}Cu_{2}B_{10}$	11	bcc + fcc	–	1960	3.3	
$Fe_{68}Co_{5}Cr_{10}Ni_{5}Cu_{2}B_{10}$	4	bcc + fcc	–	2570	3.4	
Amorphous materials						
$Fe_{80}P_{16}C_{3}B_{1}$	5	Amorphous	–	2000 to 3000	–	[34]
	8		–	1000	–	
$Fe_{80}B_{20}$	4	Amorphous	–	2200	2.7	[38]
$Fe_{76.5}Si_{8.5}B_{15}$	3		–	3100	2.7	
$Fe_{68}Si_{17}B_{15}$	4		–	3600	3.6	
$Fe_{65}Cr_{10}Si_{10}B_{15}$	5		–	3800	4.1	
$Fe_{65}Co_{10}Si_{10}B_{15}$	9		–	4400	3.8	
$Ni_{20}Fe_{60}B_{20}$	7	Amorphous	–	3100	2.5	[43]
$Ni_{25}Fe_{50}Si_{10}B_{15}$	12		–	2500	3.7	
$Ni_{25}Fe_{50}Si_{10}B_{15}$	6		–	1700	3.0	
$Ni_{80}P_{20}$	6		–	1800	2.7	
$Fe_{80}P_{20}$	12		–	1900	2.8	
$Ni_{60}Fe_{20}P_{20}$	6		–	1700	2.1	
$Ni_{60}Fe_{20}P_{20}$	15		–	1900	2.7	
$Ni_{60}Fe_{20}P_{16}B_{4}$	5		–	1900	2.0	
$Ni_{20}Fe_{60}P_{16}B_{4}$	5		–	1700	2.3	
$Ni_{75}P_{15}Si_{10}$	6		–	1900	2.8	
$Ni_{50}Fe_{25}P_{15}Si_{10}$	8		–	1000	1.1	
$Ni_{25}Fe_{50}P_{15}Si_{10}$	6		–	2600	2.2	

*Glass coating not removed prior to testing.

(c) The viscosity–temperature behaviour of the glass must allow easy fibre drawing in the temperature range of interest.

(d) The glass should not normally crystallize during the drawing operation, i.e. the crystallization temperature of the glass must be significantly greater than its working temperature.

(e) The thermal expansion coefficient of the glass should be matched to, or be slightly less than, that of the metal or alloy of interest otherwise, during cooling, thermal stresses will be generated within the glass; if these are high enough, failure and fragmentation of the glass coating will occur and may prevent drawing of continuous filament.

(f) The viscosity of the glass coating must attain a high enough value, where further extension during drawing cannot occur, before the metal core has solidified; otherwise, if the core is solid and the coating continues to extend, fracture of the metal core will be initiated and a discontinuous product obtained. If this cannot be easily controlled by materials selection, the process parameters must be adjusted accordingly (See Section 2.1.3.2 (f)).

In practice, because glass is used in the form of tube of uniform dimensions in the Taylor-wire process, the choice of specific glass composition is severely restricted due to the very limited range of glasses that are commercially available in this form. In general, this restricts the choice of glass to a number of low thermal expansion, Pyrex-type borosilicate compositions, or to fused silica.

2.1.3.2. Process conditions.

(a) It is important that the starting materials are thoroughly cleaned prior to use. Ideally this will involve a degreasing and vacuum-annealing stage. Failure to clean glass and metal adequately will result in filament of low quality due to the evolution of gases at the metal–glass interface.

(b) The molten metal within the glass tube should be protected by an inert atmosphere during drawing, otherwise excessive oxidation of the metal may occur which could prevent the drawing of continuous filament.

(c) It has been reported that induction heating employing the levitation principle is particularly useful for obtaining stable melt-drawing conditions.

(d) The most important factor governing the core diameter of a filament seems to be the take-up speed; the higher the speed, the smaller the fibre dimensions obtained. Other factors do, however, play a secondary role, including the initial diameter of the glass tube, the feed-in rate of glass and metal feedstock into the heating zone, the melt temperature, and the cooling rate achieved.

(e) The thickness of glass coating obtained depends mainly on the feed-in rate of the glass tube, but also depends to a lesser degree on the thickness of glass tube employed, and the take-up speed.

(f) The most important factor for obtaining a continuous filament appears to be the cooling rate, which can be varied not only through variation of the drawing parameters, but also by incorporation of an additional cooling device after the heating zone. Filament quality, in particular its continuity, improves with increasing cooling rate.

2.1.4. Properties of microwires produced by the Taylor-wire process

2.1.4.1. Mechanical properties and microstructure. One of the earliest reports dealing with the mechanical properties of microwire is that of Soltis [11] of the Naval Air Engineering Center in the USA. He measured the strength of copper microwires supplied by Glass Developments Ltd in the UK, after removal of the glass coating in aqueous HF solution. He noted that the highest strengths, up to 2500 MPa, were obtained with very fine wires, ~ 1 μm in diameter.

Manfrè *et al.* [23] have also reported the results of mechanical property measurements that they carried out on copper microwires prepared in their own laboratory. In addition, they have given details of the microstructures of the resultant materials. They noted that the microwires exhibited polycrystalline structures consisting of single-crystal grains aligned with their [1 0 0] axes almost parallel (to within ~ 15°) to the fibre axis. The precise texture and grain size depended on the drawing ratio and quench rate. Higher cooling rates were found to yield smaller grain sizes for a given wire diameter, with values ranging from ~ 1 to 8 μm, and with single-crystal grains often extending across the whole width of a wire. Typical values for the tensile strength of filaments after removal of the glass coating in aqueous HF solution were 50 to 180 MPa, with total elongations to failure of ~ 8 to 15%. Some values for specific materials are summarized in Table III.

If the data of Manfrè *et al.* [23] for yield strength and ultimate tensile strength are plotted against fibre diameter, the scatter is high. If, on the other hand, the data are plotted against the grain size, a much tighter dependence is noted, as shown in Fig. 5, indicating that grain size is the important parameter in determining the strength of these materials.

Comprehensive fibre texture details have been reported by Bunge [25] for a number of metal and alloy microwires produced by the Taylor-wire route. Some of these data are summarized in Table III.

Systematic data have also been published by Gotō and co-workers for the mechanical properties and microstructures of a number of materials produced by the Taylor-wire route. Mechanical properties were measured after stripping of the glass coating. The materials studied included copper [31], silver [33], gold [36] and iron [31], and a number of iron-based [34, 38, 48, 49], nickel-based [39, 43], copper-based [37, 40–42] and lead-based [44–47] alloys. The authors noted that, in general, a broad trend of increasing tensile strength and decreasing elongation to failure with decreasing fibre diameter was obtained, as summarized in Table III and Fig. 6. It should be emphasized that their data exhibited a considerable degree of scatter, although this is not surprising in view of the difficulties associated with the mechanical testing of fine fibres and the variability in damage to fibres that must occur during stripping of the glass coating. Only limited data were given on the grain sizes of the resultant materials. Strengths in excess of 3000 MPa were achieved for many of the iron-based alloys, with an ultra-high strength of 4400 MPa being found for an $Fe_{65}Co_{10}Si_{10}B_{15}$ amorphous fibre 9 μm in diameter [38].

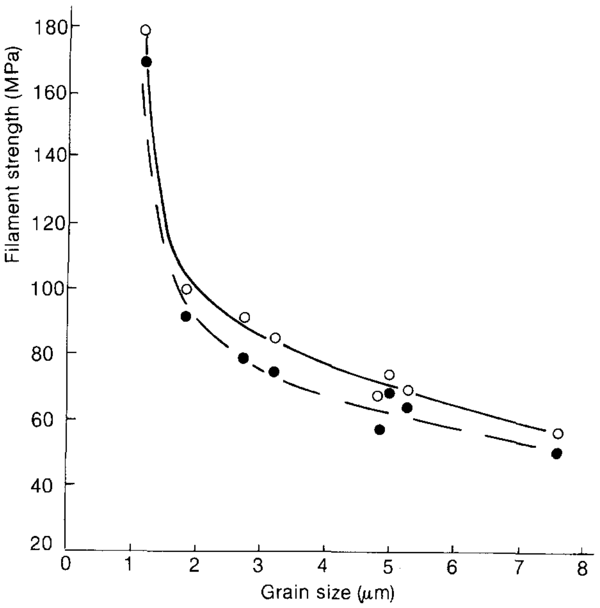

Figure 5 (●, ---) Yield strength and (○, ——) ultimate tensile strength of copper filament produced by the Taylor-wire process as a function of grain size; after Manfrè *et al.* [23].

With the exception of some of the iron- and nickel-based alloys [34, 38, 43], which were obtained in an amorphous state under certain drawing conditions, the majority of the materials reported by Gotō and co-workers were microcrystalline and exhibited a high degree of fibre texture which increased with increasing drawing speed. For example, with copper filaments a single [1 0 0] texture was observed [32], and for iron a single [1 1 1] texture was noted [32]; for silver, on the other hand, a single [1 0 0] or a double [1 0 0] + [2 2 1] texture was found [33], depending on the precise drawing conditions. These results are summarized in Table III.

The mechanical properties of glass-coated microwire prepared by the Taylor-wire technique have also been measured in the author's laboratory [54]. In this case, the glass cladding was not removed prior to testing. Depending on the fibre diameter and coating thickness, tensile strengths of up to ~ 1250 MPa were obtained, with failure strains up to ~ 2.5%. The failure

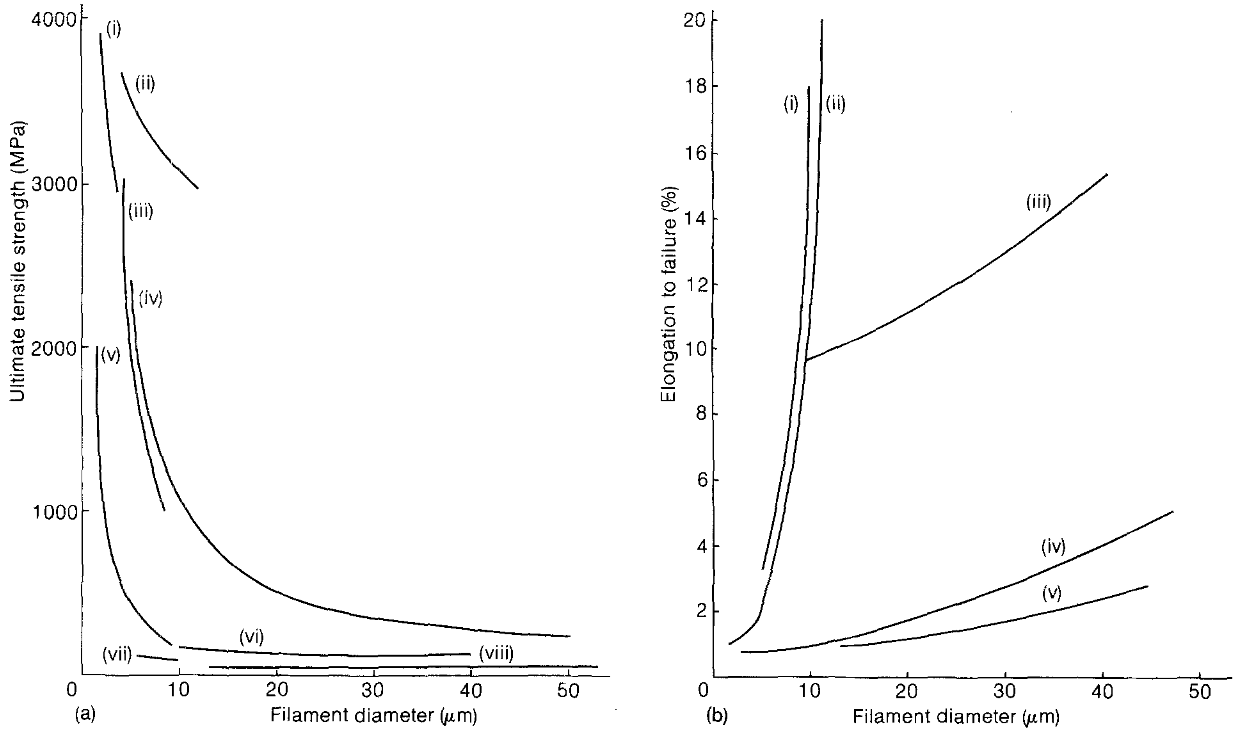

Figure 6 (a) Ultimate tensile strength, and (b) elongation to failure as a function of filament diameter for a number of metals prepared by the Taylor-wire route; after Gotō and co-workers [31, 34, 38, 41, 47, 48] and Manfrè *et al.* [23]. (a) (i) Fe–B alloy, (ii) Fe–Co–Cr–Mo–B, (iii) Fe–P–C, (iv) iron, (v) copper, (vi) copper, (vii) Cu–V–Si–Ge, (viii) Pb–Bi–Ge. (b) (i) Cu–V–Si–Ge, (ii) copper, (iii) copper, (iv) iron, (v) Pb–Bi–Ge.

mode of these fibres is very interesting. For thin cores with relatively thick glass coatings, failure of the core occurs catastrophically immediately after the failure strain of the glass cladding is reached. The fracture surface in this case is relatively featureless, as shown in Figs 7a and b. If, on the other hand, the core is large relative to the overall fibre diameter, the core continues to support a load after the failure strain of the cladding has been reached. This gives rise to a more controlled failure mechanism, with extensive plastic deformation and necking-down of the core together with spalling of the glass cladding, as shown in Figs 7c and d.

2.1.4.2. Other material properties. Amorphous ferromagnetic Fe–P–C-based microwires have been prepared by Wiesner and Schneider [24] using the Taylor-wire technique. Values of saturation magnetization for these wires of ~ 10 to 14 kG were noted, depending on the precise composition, and this is of the same order as that obtained for Fe–P–C amorphous alloys prepared by more conventional rapid-quenching routes. Coercive force was, however, noted to be relatively low at ~ 0.12 to 0.18 Oe.

Gotō and co-workers have prepared ductile microcrystalline microwires based on copper [40–42] and lead [44–47] which exhibit superconducting properties, with transition temperatures of above 10 K. Some of their data are summarized in Table IV.

Electrical resistivity measurements have also been reported by Miroshnichenko *et al.* [19] and Bashev [20] for amorphous and microcrystalline Fe–C–B and Fe–C alloys.

2.2. Other techniques for producing metallic filaments directly from the melt

In addition to the Taylor-wire process, a number of other methods have been devised for producing fine metallic filaments of circular cross-section directly from the melt. Some details of these methods follow.

2.2.1. Free-flight melt-spinning into a gaseous environment

Several techniques have been reported for the preparation of microwire in which molten metal or alloy is ejected through a fine orifice into a gaseous environment. Under suitable conditions it is possible to maintain a stable stream of molten material, which subsequently solidifies to form a solid filament. In order to prevent the stream from breaking up into droplets under the action of surface tension forces or turbulence before solidification has occurred, however, the process and materials conditions must be very carefully selected and controlled.

For example, in the method of Pond [55], a melt is ejected under gas pressure through a nozzle into a chamber containing an inert atmosphere. The method relies mainly on having an ejection velocity which is high enough to prevent or minimize stream break-up before solidification occurs. The use of a cooling gas with a high heat-transfer coefficient, for example helium, to promote more rapid solidification is highly beneficial in accomplishing this. Pond [55] claimed that the method is suitable for preparing most nonrefractory metals and alloys as filament ranging in diameter from ~ 13 μm to 8.6 mm. Other factors which influence the process include the degree of melt

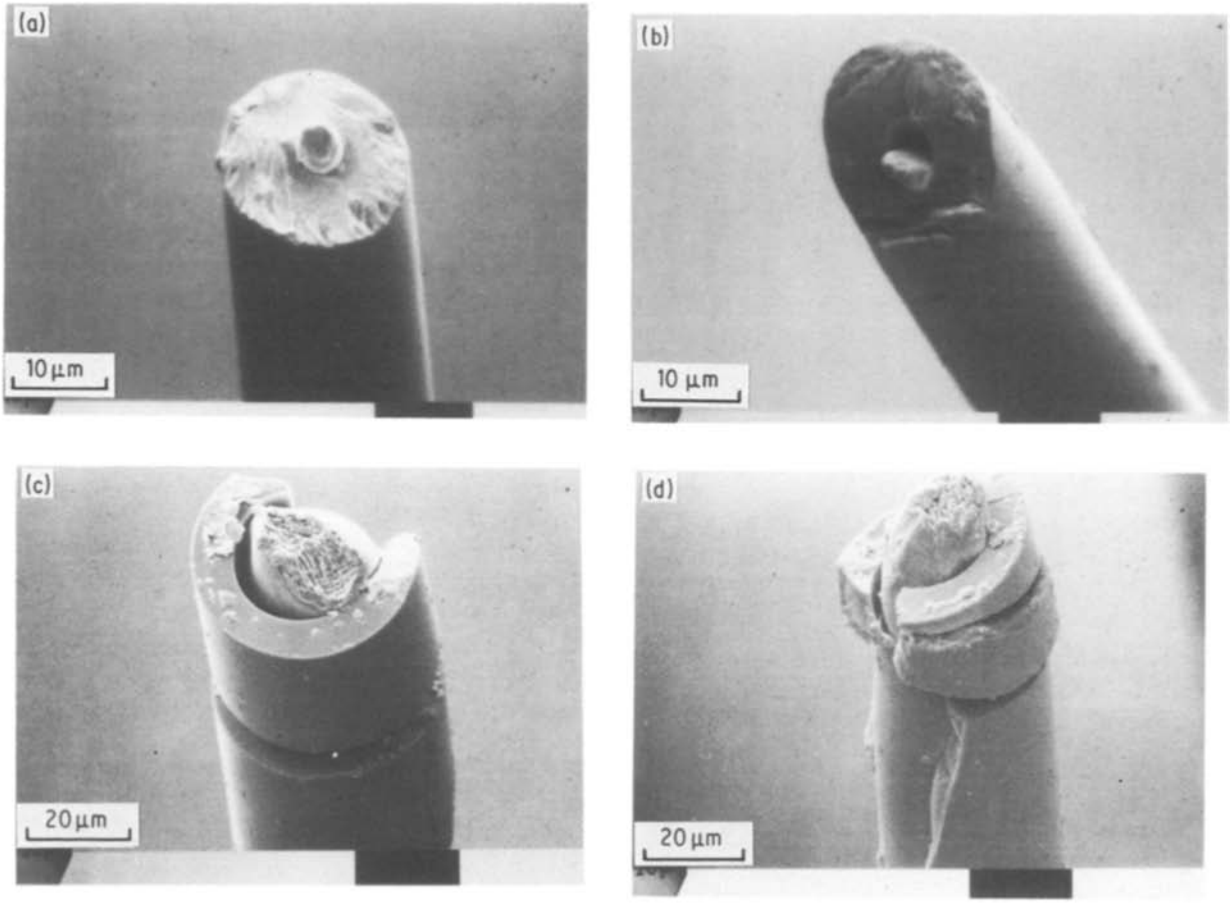

Figure 7 Fracture surfaces of glass-coated copper microwire failed in tension, after Metcalfe *et al.* [54]: (a, b) thin core, bar = 10 μm; (c, d) thick core, bar = 20 μm.

TABLE IV Properties of some superconducting microwire materials prepared by the Taylor-wire route

Material	Fibre diameter (μm)	Tensile strength (MPa)	Elongation to failure (%)	Post-drawing heat-treatment	Superconducting transition temperature (K)	Reference
V_3Si	–	–	–	As-drawn	17.0	[40]
$Cu_{93.2}Nb_{4.5}Sn_{2.3}$	10	310	3.9	600° C for 200 h	8.0	
$Cu_{93.2}Nb_{4.5}Sn_{2.3}$	12	230	5.6	600° C for 200 h	8.0	
$Cu_{95.5}Nb_3Ge_{1.5}$	10	370	3.9	As-drawn	6.1	
$Cu_{95.5}Nb_3Ge_{1.5}$	16	270	2.3	600° C for 100 h	5.5	
$Cu_{86.5}V_{10.1}Si_{3.4}$	9	–	–	As-drawn	5.8	[41]
$Cu_{86.5}V_{10.1}Si_{3.4}$	9	–	–	500° C for 600 h	11.0	
$Pb_{50}In_{50}$	66	20	2.5	–	6.2	[44]
	36	–	–	–	6.6	
$Pb_{85}Bi_{15}$	49	40	3.8	–	7.9	
$Pb_{75}In_5Bi_{20}$	53	40	3.0	–	10.2	[45]
$Pb_{70}Sn_{10}Bi_{20}$	71	30	3.4	–	9.5	
$Pb_{80}Bi_{20}$	43	50	2.9	–	11.0	
$Pb_{52}Sn_{20}Ge_{28}$	24	51	3.7	As-drawn	8.6	[46]
$Pb_{49}Bi_{23}Ge_{18}$	13	20	0.9	As-drawn	10.8	[47]
$Pb_{49}Bi_{23}Ge_{18}$	21	20	1.4	As-drawn	13.0	
$Pb_{49}Bi_{23}Ge_{18}$	44	20	2.7	As-drawn	14.3	
$Pb_{53}Bi_{26}Ge_{21}$	44	250	0.8	As-drawn	11.4	[47]
$Pb_{53}Bi_{26}Ge_{21}$	55	240	1.1	As-drawn	13.0	
$Pb_{57}Bi_{22}Ge_{21}$	41	230	1.3	As-drawn	11.4	[47]
$Pb_{57}Bi_{30}Ge_{13}$	62	240	1.4	As-drawn	11.2	[47]

TABLE V Properties of some microwire materials prepared by the Monsanto free-flight melt-spinning technique (after [58–60])

Material	Casting atmosphere	Stabilizing film	Fibre diameter (μm)	Ultimate tensile strength (MPa)	Elongation to failure (%)
Cu	0.27 atm. CS_2	Carbon	80	95	22.0
Au	1 atm. C_3H_8	Carbon	50	–	–
Be	17.3% O_2 + 82.7% Ar	BeO	–	–	–
U	1 atm. N_2	UN_2	100	–	–
Sn	67% He + 33% O_2	–	85	–	–
Mn	0.39 atm. CS_2	MnS_2 or carbon	100	–	–
B	90% N_2 + 10% NH_3	BN	115	690	–
Stainless steel	80% N_2 + 20% O_2	–	90 to 100	–	–
Al–Zn alloy	17.3% O_2 + 82.7% Ar	Al_2O_3 + ZnO	85	275	3.5
Al–Mg–Cu–Mn alloy	0.07 to 1.0 atm. O_2	Al_2O_3	100	115	26.8
Ni–Cr–Al–Fe alloy	80% N_2 + 20% O_2	Al_2O_3	37	480	9.8
Al_2O_3–CaO	1 atm. C_3H_8	Carbon	200	725	–

superheat, the surface tension and viscosity of the melt, and the density of metal or alloy under consideration.

A more successful method of achieving stable jet conditions, according to Alber and Smith [56], is to employ an alloy which will form a stable, more refractory oxide that is insoluble in the molten metal. Suitable alloys are ejected into an oxidizing environment and, under appropriate conditions, a solid oxide film forms over the molten alloy stream. This stabilizes the stream and prevents it from breaking up before solidification of the alloy itself has occurred. It was claimed that alloy microwires based on copper, silver, gold, platinum, iron, nickel, germanium, indium, cobalt and manganese, with small additions of aluminium, magnesium, beryllium, chromium or lanthanum, could be prepared by this technique with diameters of less than 50 μm. The lower size limit is set by the minimum orifice dimension that can be achieved in a suitable containment crucible.

Shepel'skii and Zhilkin [57] have also reported the preparation of copper and aluminium metal fibres by ejection of molten metal through a relatively fine ($\sim$ 0.2 mm diameter) fused silica nozzle into air. Optimum ejection pressures of 1.5 and 2.15 m sec^{-1} for copper and aluminium, respectively, were found to yield continuous fibre of high quality. The presence of an oxide film presumably aided in melt-stream stabilization.

The idea of providing a stabilizing film encapsulating the melt stream has been pursued and expanded by workers at the Monsanto Co. [58]. Their basic method consists of ejecting molten material into a gaseous environment which is chosen according to the characteristics of the metal used. Under suitable conditions, reaction with the atmosphere occurs to give a stabilizing film over the surface of the melt stream, prior to solidification. For example, alloys containing aluminium, when spun into an oxygen-containing environment, form a protective film of Al_2O_3 which stabilizes the melt stream. Alternatively, these alloys may be spun into an atmosphere which contains ammonia or hydrogen sulphide where reaction occurs to give a film of aluminium nitride or aluminium sulphide. Other metal filaments, including stainless steels, beryllium, copper, gold, tin and uranium have been produced successfully using this technique, by employing appropriate atmospheres, in diameters down to $\sim$ 40 μm. In addition, it was claimed that boron filaments could be produced by spinning into an ammonia-containing atmosphere; a protective film of boron nitride is responsible for jet stabilization in this instance. Details of various fibres which have been prepared using the Monsanto free-flight melt-spinning technique are summarized in Table V. The method was subsequently improved [59, 60] by the introduction of a countercurrent or co-current gas flow within the spinning chamber.

2.2.2. Free-flight melt-spinning into a liquid environment

In addition to free-flight melt-spinning into a gaseous atmosphere, it is also feasible to spin into a liquid environment. For example, Engelke [61] reported a method in which he claimed that metallic filaments could be prepared by ejecting molten metal through a fine orifice into a compatible liquid medium that surrounds and flows with the molten metal stream, as illustrated schematically in Fig. 8. The containment liquid is pumped through a tube surrounding the ejection nozzle, and it is important that stable (i.e. laminar) liquid flow is maintained; if turbulent flow conditions are allowed to develop a discontinuous product is obtained. By changing the size of the orifice through which molten metal is ejected, and the rate of flow of the surrounding liquid, the diameter of the filament produced can be varied over the range $\sim$ 25 μm to 3 mm. It was suggested that molten NaCl or KCl could be used as a containment fluid for metals with melting points of the order of 1000° C. It was claimed that the method could also be used for producing non-metallic inorganic filaments, provided that a suitable compatible containment fluid could be identified for the material in question. No details or properties of specific materials produced by the method were disclosed.

A related technique, in which molten material is ejected through an orifice into a liquid medium which flows with the molten stream, has been developed by Kavesh [62]. In this method, the molten metal or alloy is contained in a fused silica or zirconia crucible containing one or more tapered orifices 20 to 600 μm in diameter. Molten material is ejected by gas pressure across a small air gap into a circulating quenching medium where it solidifies to produce filament of circular cross-section. The quenching medium may be

TABLE VI Details of materials produced by melt-spinning into liquid, after Kavesh [62]

Material	Fibre diameter (μm)	Quenching medium	Quenching temperature (°C)
Mg	203	Water	1
Al	127 to 152	Water	10
Si	152	Aqueous $ZnCl_2$ (51 wt %)	-62
Mn	152	Aqueous $MgCl_2$ (21.6 wt %)	-33
Fe	152	Aqueous $ZnCl_2$	-62
Co	152	Aqueous $ZnCl_2$	-62
Ni	152	Aqueous $ZnCl_2$	-62
Cu	152	Aqueous $MgCl_2$	-33
Pd	254	Aqueous $ZnCl_2$	-62
Ag	635	–	–
Sn	152 to 305	Water	1 to 20
Au	152	Aqueous NaCl (23.3 wt %)	-20
Pb	152	Water	1 to 20
Ti–Al–V alloy	152	Aqueous $ZnCl_2$	-62
Zn–Al–Cu alloy	305	Water	10

water or an aqueous chloride solution. In principle, filaments may be obtained with diameters down to $\sim 20\,\mu$m. Details of some specific materials produced by this method are summarized in Table VI.

More recently, Ohnaka *et al.* [63] at Osaka University have developed a melt-spinning technique in which molten alloy is ejected through a fine nozzle into a water layer held, by centrifugal force, on the inner surface of a rotating drum. The technique is illustrated schematically in Fig. 9. The diameter of wire obtained is mainly a function of the diameter of the ejection orifice. The shape of the wire cross-section depends on the angle of incidence of the jet stream to the water surface; a circular cross-section is obtained for small incidence angles, whilst larger angles lead to elliptical fibres. The cooling rate achieved during the process has been estimated [64] to be of the order of $10^5\,K\,sec^{-1}$ for 100 to 200 μm diameter fibre. The method has been used successfully for producing both microcrystalline and amorphous wires of diameters down to $\sim 80\,\mu$m [63–68] from a variety of alloy systems, and has recently been reviewed in detail by Ohnaka [69]. Some of the materials produced by this method are summarized in Table VII.

It may be noted that a related technique has been developed independently by Raman *et al.* [70] at the Battelle Columbus Laboratories. Battelle, however, have used their technique which they describe as "the Battelle-invented rapid spinning cup", for producing a particulate rather than a filamentary product.

A number of the methods used for producing filament directly from the melt, in particular the Monsanto free-flight melt-spinning route, have also been reviewed in some detail elsewhere [71].

2.3. Other methods for producing fine filaments

In addition to the conventional mechanical drawing of individual wires to produce fine filaments below 100 μm in diameter which, as outlined earlier, is both labour-intensive and very expensive, another technique has been reported as suitable for the production of fine filaments from the solid state. This method [72, 73], which is based on an earlier idea of Wollaston [1], involves the incorporation of a number of standard die-drawn wires, up to 6 mm in diameter, with a suitable compatible metal matrix. This unit is then drawn or extruded down in a number of stages to produce fine filament, with a minimum diameter of less than 12 μm, embedded in the encapsulating

TABLE VII Properties of some microwire materials prepared by melt-spinning into-rotating-water

Material	Fibre diameter (μm)	Crystal phases present	Ultimate tensile strength (MPa)	Elongation to failure (%)	Reference
$Fe_{75}Si_{10}B_{15}$	180	Amorphous	3200	3.0	[64]
$Co_{72.5}Si_{12.5}B_{15}$	130		3400	3.0	
$Pd_{77.5}Cu_6Si_{16.5}$	150		1500	2.5	
$Fe_{77.5}P_{12.5}C_{10}$	80 to 140	Amorphous	2790	2.7	[65]
$Co_{77.5}Si_{12.5}B_{10}$			3580	3.0	
$Co_{67.5}Si_{12.5}B_{20}$			2750	2.2	
$Ni_{40}Fe_{30}Al_{30}$	100	β'	840	1.0	[66]
$Ni_{50}Fe_{30}Al_{20}$	100	$\gamma' + \beta'$	1200	15.0	
$Co_{45}Ni_{30}Al_{25}$	110	$\gamma' + \beta'$	860	5.0	
$Co_{40}Ni_{37.5}Al_{22.5}$	110	$\gamma' + \beta'$	820	7.0	
$Cu_{65}Zr_{35}$	135	Amorphous	1670	2.4	[67]
$Cu_{60}Zr_{40}$	110		1810	2.7	
$Cu_{57}Zr_{38}Nb_5$	95		2100	2.4	
$Fe_{74.5}Cr_{10}Ni_8Al_{6.5}C$	100	$\alpha + M_7C_3 + M_{23}C_6$	1550	1.0	[68]

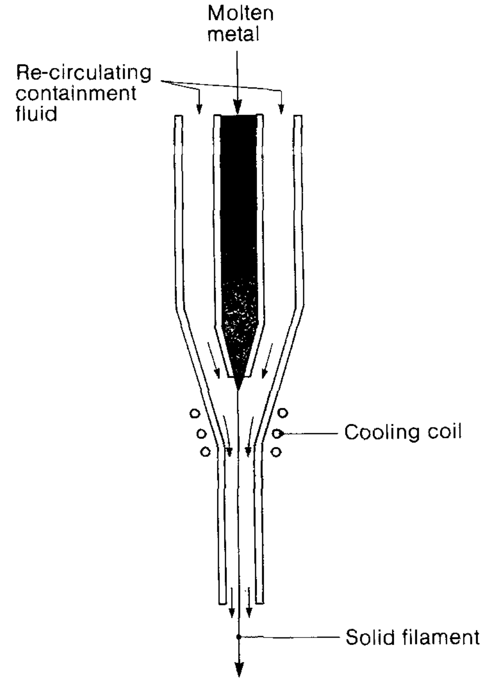

Figure 8 Free-flight melt-spinning into a liquid environment; after Engelke [61].

matrix. This matrix can then be removed chemically, for example by dissolution in a suitable acid, to leave the filament in the form of a tow. It was claimed that fine stainless steel fibres could be produced by this method using a copper or monel matrix which was subsequently dissolved in nitric acid.

A further modification to this technique was suggested by Tada *et al.* [74] in which the matrix was removed mechanically rather than chemically.

3. Methods for producing related materials

A brief summary is given of some techniques which are useful for producing related materials, including filament of non-circular cross-section and narrow ribbons, directly from the melt.

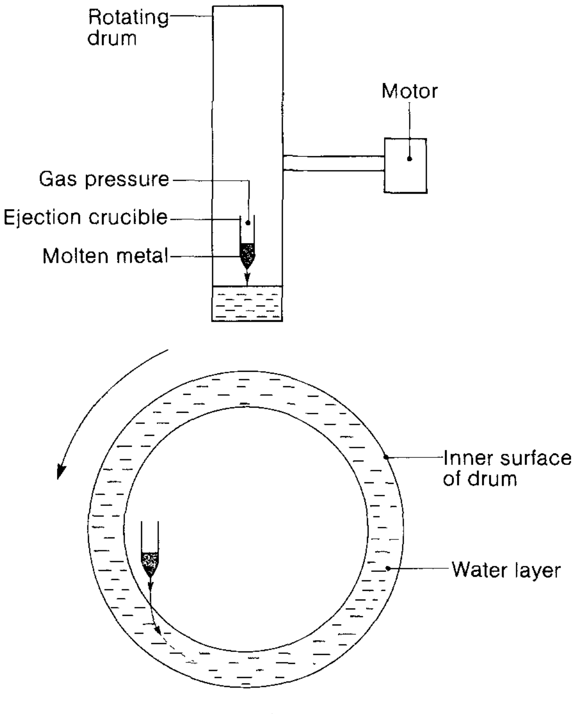

Figure 9 Free-flight melt-spinning, into-rotating-water method of Ohnaka *et al.* [63].

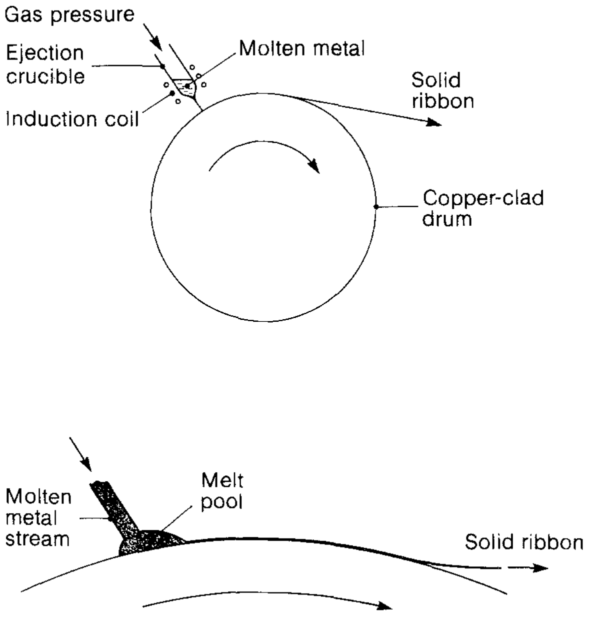

Figure 10 Chill-block melt-spinning for production of narrow ribbon.

The most versatile method of producing narrow ribbon directly from the melt is undoubtedly chill-block melt-spinning. In its simplest form, as illustrated in Fig. 10, a stream of molten metal or alloy is directed by means of a suitable nozzle on to the surface of a rapidly rotating drum, typically rotating with a surface velocity of 20 to 60 m sec^{-1}. A "puddle" of molten metal (melt-pool) is obtained at the wheel surface; the melt is therefore in intimate contact with a good heat-sink. From the underside surface of this melt-pool a solid ribbon of material is extracted. Ribbon dimensions down to $\sim 10\,\mu$m thickness and $\sim 100\,\mu$m in width can be achieved, depending on the nozzle dimensions and the process conditions. The method has been described by Pond [75] for producing microcrystalline metallic ribbons, and by Liebermann and Graham [76] for producing amorphous materials, and is based on an earlier idea of Strange and Pim [77].

A related technique for producing narrow ribbon is twin-roller casting, illustrated in Fig. 11, in which a stream of molten metal is directed through the nip of contra-rotating rollers held lightly in contact [78, 79].

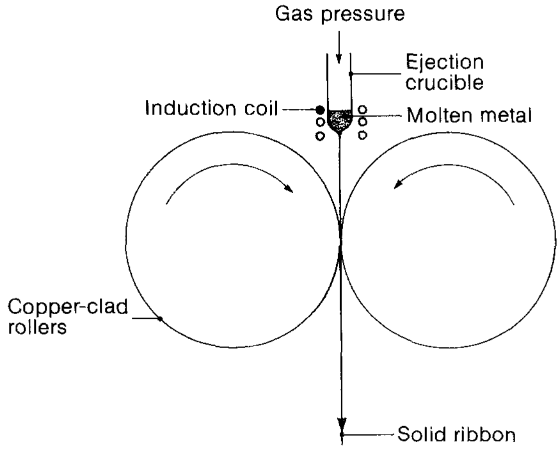

Figure 11 Twin-roller casting for preparing narrow ribbon.

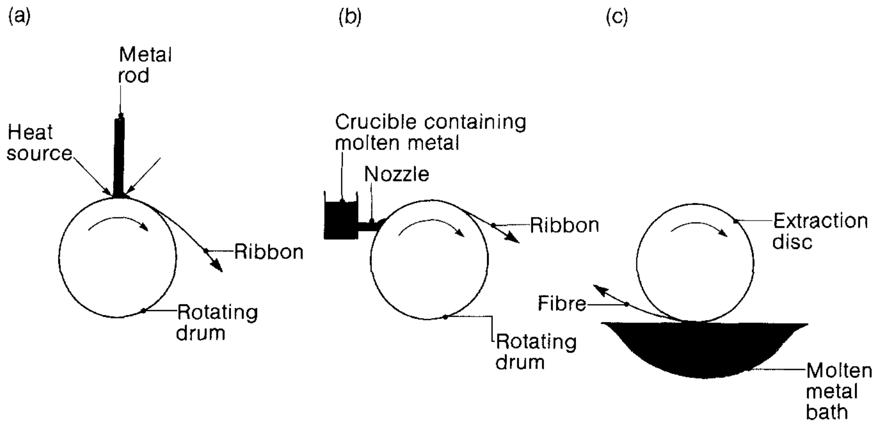

Figure 12 Other rapid-quenching techniques: (a) pendant-drop melt-extraction and (b) melt-drag for producing narrow ribbon, and (c) crucible melt-extraction for preparing fibre of kidney-shaped cross-section.

In principle, ribbons of similar dimensions to those produced by melt-spinning may be obtained. A comparison between the two methods has been made by Lewis *et al.* [80] and, in general, melt-spinning is noted to produce ribbon of higher quality.

Narrow ribbon may also be produced using pendant-drop melt-extraction [81] or melt-drag [82, 83], whilst fibre of kidney-shaped cross-section has been produced by crucible melt-extraction [81]. These methods are illustrated in Fig. 12. These and other rapid-quenching methods have been reviewed in more detail by a number of authors (e.g. [26, 27, 50, 84–88]).

4. Methods of glass-coating fine metallic filaments

Of all the methods available for producing microwire and related materials, only the Taylor-wire process offers a technique for producing fine glass-coated filaments directly from the melt. Although the glass-coating may be a disadvantage for some applications, it is highly desirable for applications where an electrically insulated filament is required. The method is not, however, too successful with certain metals, in particular reactive species like beryllium, or with refractory metals, including molybdenum and tungsten. Consequently, a number of methods have been derived for glass-coating existing die-drawn metal filaments of diameter down to around 25 μm.

For example, McMillan and co-workers [89, 90] have given details of a method that they employed for glass-coating suitable metal filaments which involved drawing wire through molten glass held on a series of heated metal support loops. The process is illustrated in Fig. 13a. The method was reported as suitable for coating a number of metal wires, including chromel and alumel alloys used in thermocouples, with a variety of glasses of varying thermal expansion characteristics. Suitable glasses included compositions from the $BaO–B_2O_3–SiO_2$ system. Other compositions from the $BaO–ZnO–P_2O_5$ phase field, after application to a metal filament whilst in the glassy state, were noted to be suitable for further heat-treatment to produce a more refractory glass–ceramic coating.

Miriam [91] of Glass Developments Ltd in the UK has also patented a device for glass-coating metal wires. In his method, metal filaments 25 to 100 μm in diameter were coated directly with glass by feeding the wire through a glass tube which was softened at one end by gas flames. By varying the wire and glass tube feed-through rates, in addition to the glass temperature, it was claimed that various coating thicknesses could be achieved. In principle, this method, illustrated in Fig. 13b, is somewhat similar to the Taylor-wire technique, with the exception that in Miriam's method the metal is not melted.

Comprehensive details have also been given by Potter and Henning [92] of methods that they have adopted for glass-coating a selection of fine metal wires. Filaments of tungsten, beryllium and copper, in thicknesses down to ~ 25 μm, were successfully coated using a number of commercially available glasses, including medium thermal expansion soda–lime and potash–soda–lead compositions, and low-expansion borosilicate types.

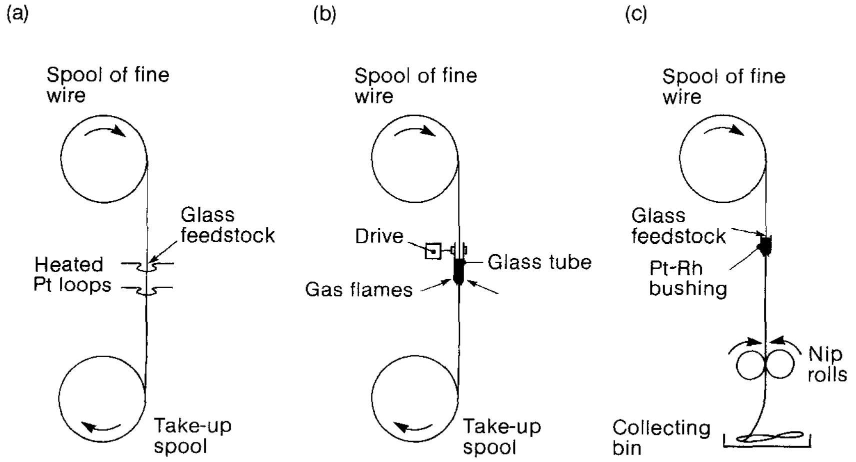

Figure 13 Methods employed for glass-coating of fine metal filaments: (a) method used by McMillan *et al.* [89, 90], (b) method used by Miriam [91], (c) method used by Potter and Henning [92].

Spooled wire was fed through a glass tube on to a take-up drum; a small electrically heated furnace was employed to soften the glass at the end of the tube. Wire was then pulled through the molten zone at a preselected rate, whilst the glass tube was fed slowly into the furnace. This method is therefore somewhat similar to that employed by Miriam [91]. The second method, shown in Fig. 13c, utilized a heated Pt–Rh alloy bushing through which wire was pulled whilst molten glass was metered to the bushing via a platinum tube. Filaments were successfully coated in air by both methods, no serious oxidation problems being apparent.

5. Comparison of methods for producing microwire and related materials

For the production of fine glass-encapsulated metallic filaments down to $\sim 1\,\mu$m in diameter, the Taylor-wire process offers the only practical solution. Its major disadvantage is that for certain applications a glass coating may be undesirable and therefore may have to be removed prior to use. This will tend to increase the cost of such material, and may lead to damage of the wire during the stripping process. In principle, any metal or alloy, in addition to certain ceramics, can be produced in microwire form using the Taylor-wire method, providing that a suitable compatible glass can be found. Difficulties can, however, be associated with the use of very reactive metals, for example beryllium or Group IVa elements, and also with refractory metals, due to reaction with the glass at the temperatures involved, although these difficulties are not insurmountable. In addition, glass choice is normally restricted to the compositions that are readily available commercially in a suitable form; for example, certain low-expansion borosilicates or fused silica. Because very high cooling rates, $\geqslant 10^5\,\mathrm{K\,sec^{-1}}$, can be achieved using the Taylor-wire process, it is also feasible to produce certain alloys of potential interest in the form of amorphous microwires. The Taylor-wire route is hence an extremely versatile and intrinsically inexpensive means for producing a variety of microwires of circular cross-section in the range $\leqslant 1\,\mu$m to $\sim 100\,\mu$m diameter.

Other methods which involve quenching from the melt to produce microwire of circular cross-section, for example free-flight melt-spinning into a gaseous [55–60] or liquid [61–69] environment, are more ideally suited for preparing filament of diameter above $50\,\mu$m and ideally $\geqslant 100\,\mu$m. All these methods rely on ejecting molten material through a fine orifice, and are limited both by the availability of suitable fine nozzles, and by the very stringent process conditions required to prevent stream break-up before solidification has taken place. One particularly interesting method, however, appears to be the technique developed by Ohnaka *et al.* [63] which involves ejecting a molten metal stream into a rotating water layer.

Fine filament of circular cross-section can also be produced by solid-state techniques which involve the mechanical drawing of either a single filament or a number of filaments contained in a suitable deformable and compatible matrix [72–74]. These methods are, however, extremely expensive and are not generally applicable to the large-scale production of individual filaments, although they have been used commercially for producing small quantities of material.

Other rapid-quenching techniques from the molten state are suited for producing materials of non-circular cross-section, for example narrow ribbon [75–83] or fibre of kidney-shaped cross-section [81], with minimum dimensions down to $\sim 10\,\mu$m thick and $\sim 100\,\mu$m wide for ribbon, and $\sim 50\,\mu$m diameter for fibre.

6. Applications for microwire

Microwires produced directly from the melt by the Taylor-wire process are intrinsically inexpensive relative to materials produced by the more conventional route of mechanical die-drawing. There has, however, been a general lack of commercial interest in microwire due in part to the unfamiliarity of design engineers with the availability and properties of microwire, and also due to the prohibitively high cost associated with the more familiar conventionally produced materials. The excellent mechanical or electrical properties of microwire, coupled with the intrinsically low cost of Taylor-wire produced material, suggests however that they could be usefully employed in a number of interesting applications, as summarized below.

6.1. Electrical materials

A great advantage of material prepared by the Taylor-wire process is that it is automatically produced with a thermally resistant, electrically insulating coating, free from discontinuities, pinholes or other defects which might impair its electrical characteristics. Such microwires have apparently been used successfully in the USSR [3] for a number of electrical applications. For example, as miniature wire-wound resistors, fast-response fuses, precision high-voltage dividers, and resistance coils for galvanometers and related devices, employing copper or manganin alloy microwires. Other potential electrical applications include miniature thermocouples and resistance thermometers and in miniature motors. Methods by which connecting leads can be attached to microwire have been reported by Litvinenko *et al.* [93].

It has also been reported [40–42, 44–47] that ductile superconducting filaments less than $60\,\mu$m in diameter have been prepared by the Taylor-wire process, with superconducting transition temperatures of above 10 K. Conventional superconducting filaments are expensive to produce, and are generally brittle and hence limited in their applications.

6.2. Composite materials

There is an increasing demand for high-performance composite materials for use in a diverse range of applications. In particular, ceramic-matrix composites, toughened by suitable fibre additions, are ideal candidates for use in aerospace applications, including turbine components and thermal and ballistic protection shrouds, and also for biomedical materials [94, 95]. In general, however, simultaneous strengthening and toughening of a ceramic can only be accomplished successfully by incorporation of very fine fibres, ideally much less than 50 μm in diameter. Although a considerable amount of effort has gone into the study of ceramic-matrix composites over the years (e.g. [94–99]), it is only relatively recently that suitable fine fibres, other than carbon, have become commercially available, and simultaneous increases in both strength and fracture toughness of composites have been achieved. Suitable fibres include SiC and Al_2O_3, with diameters down to $\sim 12\,\mu$m, but these are still relatively expensive in continuous form and are not suited for incorporation with all types of ceramic matrix. Ductile metal fibres offer many advantages over ceramic fibres [94] and very high values for the work of fracture can be achieved using such filaments [99]. Strengths have usually been only marginally improved, however, because fibre diameters have been limited to more than 50 μm. Taylor-wire produced filament with diameters down to $\sim 1\,\mu$m therefore offers an ideal reinforcement agent for many ceramic matrices. Typically, filaments can be prepared from certain iron- and nickel-based alloys with tensile strengths above 3000 MPa, and up to 4400 MPa [38] with moderate ductility.

For the reinforcement of many ceramic matrices, including glasses, glass–ceramics and certain oxides, the thin glass coating associated with Taylor-wire is probably not a disadvantage and need not be removed prior to composite fabrication; in fact, high volume percentage fibre composites could be prepared directly from Taylor-wire, the glass coating providing the basis for a suitable matrix.

6.3. Other applications

Other applications in which microwire may be useful include filters, screens and catalysts, and also fine vernier wires for optical instruments. In addition, the Taylor-wire process offers an ideal method for producing certain amorphous materials in the form of fine filaments of circular cross-section below 50 μm in diameter, not feasible by other rapid-quenching techniques; and such filaments are ideally suited for the detailed study of materials properties, including mechanical and electrical behaviour.

Acknowledgement

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