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Fine fibres by melt extraction

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Abstract

Methods for manufacturing fine fibres of metals and ceramics below 20 μm diameter are described. Some analysis of the fabrication process is given as well as a description of properties of the fibres. A brief account is also given of selected applications of the materials.

1. The fabrication technique

Melt-quenching techniques have been considerably refined over the past two decades and industrial production of high quality amorphous metal is now routine. However, the ribbon form in which this material is usually sold does offer limitation and inconvenience in use and, perhaps because of this, some effort has been devoted to casting the material into the shape of wire or filaments of circular or near-circular cross-section.

One approach, adopted by the Unitika Corporation [1], is to cast the material into water, subsequently drawing it down to the desired diameter, perhaps as low as 10 μm, or else drawing the liquid metal in a Pyrex glass tube [2]. An alternative approach, pioneered by Maringer and Mobley [3], is to use a sharpened wheel to perform melt extraction on a pendent drop melted by an electron beam or an acetylene torch. The latter technique offers the great advantage that the material is directly cast into its final form without making contact with any third substance; however, the method apparently was only reliable down to a diameter of about 20 μm [4].

At McGill we have succeeded in using the melt extraction technique to manufacture in a continuous manner rapidly solidified fibres of various liquids in diameters down to the order of a few microns [5–7]. Figure 1(a) shows a schematic diagram of the apparatus used for making fibres from liquid metals. Unlike the pendent drop method, the material to be cast is introduced on to the sharpened wheel from below. The metal is first formed into a rod about 6 mm (0.25 in) in diameter. The rod passes through a loosely fitting guide made of a suitable insulating material (boron nitride works well) and is then heated by an r.f. induction coil specially shaped to partially levitate the molten tip of the rod. The combination of gravity, surface tension and electromagnetic forces forms the molten region into a fine tip from which extraction takes place. The small region of the tip is an essential feature in making fine quality fibres, as will be discussed below. With proper selection of parameters the tip is quite stable and the rod may be steadily fed on to the wheel so as to replace the material being extracted. The rate of feed determines, within limits, the diameter of the fibre. The system may be left to function automatically until the raw material is exhausted. At McGill we have left the system essentially unattended for up to 1 h. The wheel itself should be made of a reasonably durable metal of

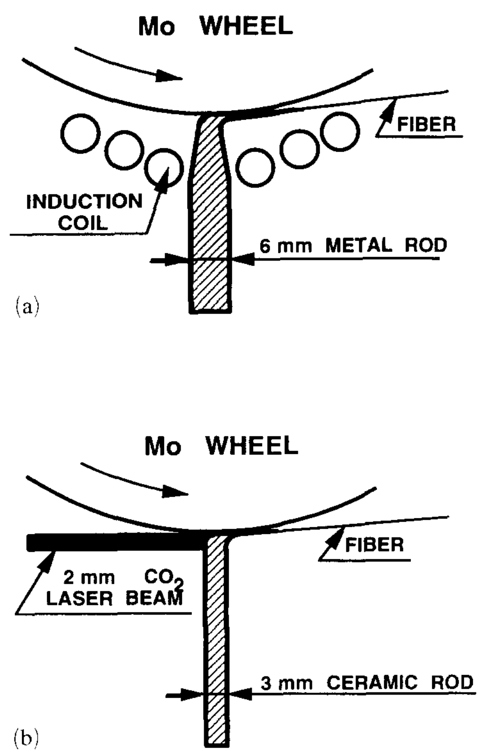

Fig. 1. Schematic diagrams of apparatus for melt extraction of (a) a metal and (b) a ceramic.

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good thermal conductivity. Copper is satisfactory for short periods by the fine tip (whose radius optimally is 5 μm or less) erodes quickly. We have found molybdenum to offer a good compromise of hardness at high temperature and sufficient thermal conductivity, though no doubt other materials would also work.

The process itself is generally carried out under a reduced pressure of some inert gas (argon, helium or nitrogen) both to eliminate oxidation problems and to control any turbulence associated with gas boundary layers.

Figure 1(b) shows a schematic diagram of the apparatus used for making ceramic fibres. The r.f. induction coil has been replaced by a 2–3 mm beam from a 180 W CO_2 laser. It is no longer possible to use electromagnetic forces to help shape the molten tip, so the ceramics rod has been made of smaller diameter, say 3 mm, so that surface tension alone may provide a fine tip. Once a stable configuration is found, the system runs more or less automatically. It should be noted that the pendent drop technique has been applied to ceramics [8] and that melt extraction from ceramics in a molten tun-dish has also been carried out [9], though the final products have different characteristics from the present fibres, indicating that the process differs in approach.

What materials may be cast by this process? The answer is essentially any liquid with sufficient wetting of the wheel and with low viscosity, ideally below 1 poise. In practice, this means that almost all liquid metals may be so treated. However, the choice of ceramics is more limited. Ceramics with high silica content are generally difficult to use. Also, wetting of metals by ceramics is notoriously poor, although it is possible in principle to get around this difficulty by using ceramic extraction wheels provided that the rate of heat removal can be maintained. Ceramics which we have successfully cast include mixtures of Al_2O_3, ZrO_2, TiO_2 and CaO as well as a wide range of ferrites and yttrium- and bismuth-based high T_c superconductivity oxides.

Figures 2–4 show examples of fibres from selected metallic and ceramic alloys. All are below 20 μm in diameter and all have an essentially circular cross-section and smooth surfaces except where the contact with the edge of the wheel is made. The circular cross-section results of course from surface tension becoming the dominant force. If the liquid has surface tension σ and density ρ and if the wheel has radius a and tangential velocity V, then the pressure due to surface tension becomes equal to the pressure due to the centrifugal force at a fibre radius r_0, where

$$r_0 = \left(\frac{\sigma a}{\rho V^2}\right)^{1/2} \qquad (1)$$

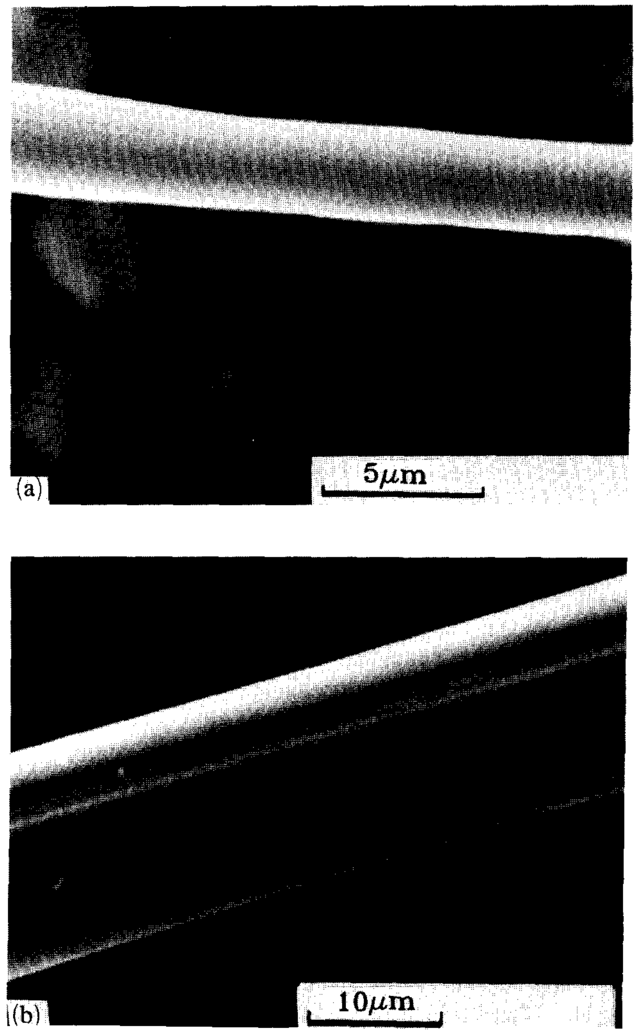

Fig. 2. Melt-extracted amorphous Ni-rich alloy (a) and Permalloy (b). Note the wheel track on the Permalloy fibre.

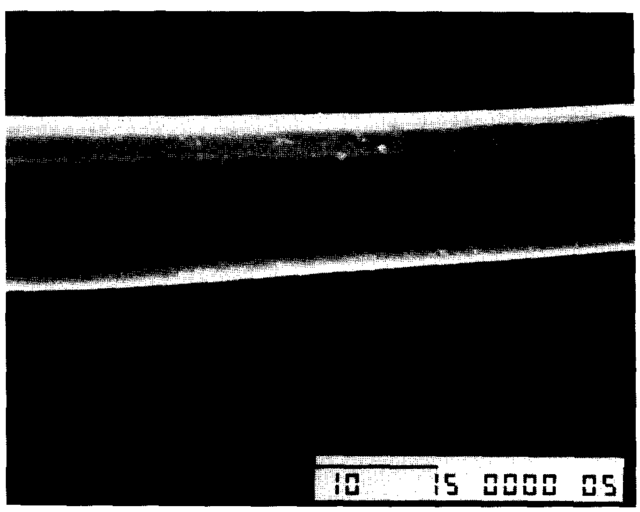
Fig. 3. Melt-extracted fibre of ZrO_2/Al_2O_3. As in Fig. 2(b), note the wheel track. Data from ref. 12.

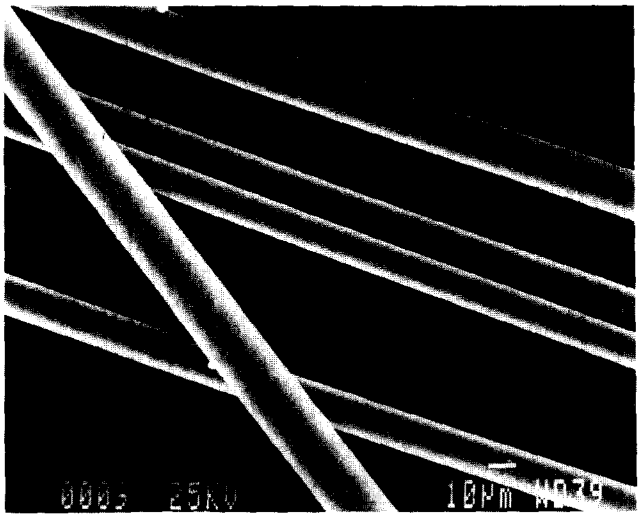

Fig. 4. Group of Al_2O_3/CaO fibres ranging from 15 to 25 μm in diameter.

Fig. 5. ZrO_2/Al_2O_3 fibre cooled too slowly to prevent Rayleigh wave formation.

Even in a "worst" case where $\sigma = 100$ dyn cm^{-1}, $V = 70$ m s^{-1}, $a = 5$ cm and $\rho = 10$ g cm^{-3}, $r_0 \approx 10$ μm, corresponding to a 20 μm fibre.

The fact that the cross-section of the fibre is a circular drop hanging from the wheel shows that the liquid solidifies after being drawn from the molten tip. If the wheel is inserted deeply into the melt, then solidification may occur before extraction and a cross-section of shape closer to the isotherms result. Under these conditions, which approximate the more familiar melt-spinning process, many of the desirable properties of the fibres mentioned below are lost. Achieving extraction before solidification is one reason why it is convenient to have the molten tip small. It also explains why 20 μm appears to be the upper limit for circular fibres, since this is determined by the viscous boundary layer (whose thickness is difficult to calculate accurately because of the temperature dependence of the viscosity).

In comparing the process of making metal fibres with that of making ceramic fibres, we note that metals show good wetting of the molybdenum wheel, have relatively low viscosities (about 10^{-2} poise), large surface tension (about 10^{-3} dyn cm^{-1}) and good thermal conductivity. All these properties help to make fabrication relatively easy, in contrast with ceramics where wetting is uncertain, viscosity larger and thermal conductivity poorer. Indeed, in quenching ceramics, the cooling process is often too slow to prevent Rayleigh waves from forming (Fig. 5).

The cooling rate in fact merits some further comment. If we compare a ribbon of thickness h with a fibre of radius r making contact with the wheel over a length l of its circumference, then, other things being equal, the ratio of quenching rate through conduction (fibre to ribbon) is of the order of $lh/\pi r^2$. Typically $l \approx 3$ μm, so that a 25 μm ribbon cools as fast by this mechanism as a fibre of 10 μm diameter, though the total quenching rate of the fibre may be significantly higher because of the greater loss of heat through surface convection (the ratio is $2h/r$). For ceramics the thermal conductivity is typically one-tenth of that for a metal or even lower and heat loss by conduction is severely reduced, though internal convective flow remains the same. In this case radiative cooling can play an important role. For a ceramic fibre of radius r at temperature T the quenching rate through radiative loss once the fibre leaves the laser beam is roughly

$$Q_R = \eta \frac{2\sigma_s T^4}{R} \frac{2}{3r} \frac{M}{\rho} \tag{2}$$

where σ_s is Stefan's constant, R is the gas constant, M is the molecular weight, ρ is the density and η is the emissivity.

For typical ceramics we have examined $\eta \approx 0.5$, $T \approx 2300$ K, $r \approx 5$ μm and $M/\rho \approx 20$. This leads to a quenching rate of about 2.5×10^5 K s^{-1}.

2. Properties

What are the advantages of using the melt extraction process given that production rates are small (even under the most favourable conditions it is hard to exceed 1 kg h^{-1} and with ceramics the rates may be considerably less)? To begin with, the process is essentially containerless, the melt being supported by the same material in the solid state. Not only does this allow access to relatively reactive metals for which finding a crucible may be challenging, it also makes the

Fig. 6. Fibre of amorphous Ba–Sr–Ca–Cu–O twisted after manufacture.

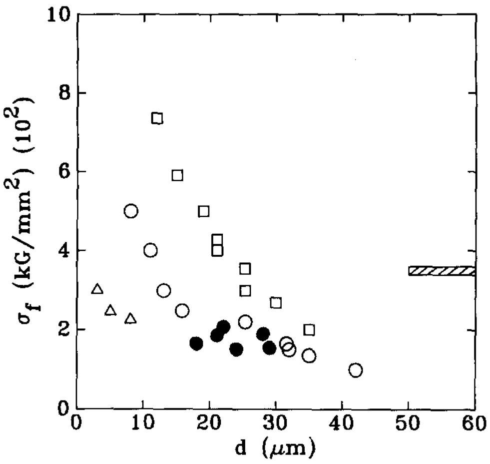

Fig. 7. Yield strength as a function of diameter: open squares, amorphous $Fe_{15}Si_{10}B_{15}$; cross-hatching, amorphous $Fe_{75}Si_{10}B_{15}$ water spun and drawn (data afrom ref. 1); open circles, crystalline $Fe_{67.5}Co_5Cr_{10}Ni_5Cu_2Mo_{0.5}B_{10}$; open triangles, $Fe_{67.5}Co_5Cr_{10}Ni_5Cu_2Mo_{0.5}B_{10}$ filaments by melt spinning with Pyrex (data from ref. 2); closed circles, ZrO_2/Al_2O_3 ceramic fibres.

fabrication of high temperature ceramics relatively easy. However, the main appeal of the fibres derives from their unusual properties. Mechanically the fibres are very flexible, even when made of very brittle materials such as ceramics. Figure 6 shows a Bi–Ca–Sr–Cu–O fibre twisted into a small loop after manufacture. Similar properties are seen for ZrO_2-, Al_2O_3-, CaO- and TiO_2-based fibres. Yield strengths are very high and increase as the diameter decreases. Figure 7 shows the behaviour of some representative fibres, with fibres produced by water spinning or melt drawing for comparison. Not surprisingly, the highest yield strengths are found for amorphous metal fibres, but even crystalline metal fibres are exceptionally strong. Ceramic fibres behave in a similar way, except that yield strengths are slightly lower.

A second valuable property of the fibres is the extraordinary enhancement of the properties of soft magnetic materials. Even high performance amorphous alloys such as Metglas 2605-S2 or Vitrovac 6025Z show significant enhancements in permeability and corresponding reductions in coercivity when cast into fibres, as seen in Table 1. (These measurements were taken with the sample in toroidal form, showing that the enhancements are basic to the material and not a result of shape effects.) More interesting is that the melt extraction technique even permits high performance magnetic materials to be made from Permalloy. Generally rapid quenching [19] has not been successful when applied to these alloys, but as seen in Table 1, melt-extracted Permalloy fibres can have permeabilities within a factor of 2 of the amorphous material, at least in ribbon form.

The reason why the fibres behave in this way is a matter for speculation. The fact that the surface is so clear and free of faults is undoubtedly a major contributor to the high yield strength and may also play a role in enhancing the magnetic performance. Also, we believe that the fibres are formed with a considerable level of quenched-in stress. When the fibre is extracted, it first cools at the tip and around the circumference, placing the still liquid core under compression. We have some indirect evidence of this from the behaviour of the Permalloy fibres. As made, they not only show good performance but also resist deterioration under mechanical deformation. When annealed, however (*e.g.* at 400 °C for 1 h), the permeability diminishes and the

Fig. 8. Permalloy fibre treated to a grain boundary etch showing the growth of crystallites away from the line of contact with the wheel.

TABLE 1. Properties of some representative soft magnetic alloys in fibre and ribbon form

Alloy	Form	d.c. permeability	d.c. coercive field (mOe)	Coercive field at 6 kHz (mOe)
Metglas 2605-S2	Ribbon (3.3 mm × 25 μm)	1.0×10^5	190	750
Metglas 2605-S2	Fibre (16 μm)	2.3 mm × 10^5	50	240
Vitrovac 6025Z	Ribbon (2.3 mm × 25 μm)	1.5×10^5	50	200
$Co_{11}Re_4Nb_2Si_{10}B_4$	Fibre (9 μm)	2.5×10^5	20	175
$Ni_{46}Co_{26}Fe_6Si_{10}B_{13}$	Fibre (7 μm)	7.5×10^4	30	160
Permalloy ($Ni_{72}Fe_{11}Cu_{13}Mo_2Mn_2$)	Fibre (16 μm)	2.8×10^4	490	750

resistance to stress disappears. We interpret this to mean that the fibres as made have so high a level of stress that any additional stress introduced by deformation is negligible. Once this stress is relieved, fibres have a similar stress sensitivity to that of conventional Permalloys.

The microstructure of the fibres is similar to that of melt-spun ribbons, varying from amorphous through nanocrystalline to microcrystalline. However, the different geometry of cooling is reflected in the stress pattern and the crystallite pattern. A good example is shown in Fig. 8, where a Permalloy fibre has crystallites growing away from the line of contact with the wheel in a generally fan-like structure.

3. Conclusions

We have shown that high quality metal and ceramic fibres of diameter below 20 μm may be made by melt extraction. The technique used differs significantly from previous melt extraction techniques and results in materials with unusual mechanical and magnetic properties. These properties make the materials attractive for application on magnetic sensors and in material reinforcement.

Acknowledgments

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