Superconductor: WIRES AND CABLES: MATERIALS AND PROCESSES

Peter J. Lee

The Applied Superconductivity Center, The University of Wisconsin-Madison

1. Introduction

The phenomenon of superconductivity was first observed in 1912 in the laboratory of Heike Kamerlingh Onnes, at the University of Leiden (Holland). At low temperatures certain materials (about 800 superconducting compounds have been recently tabulated by Poole and Farch, 2000) suddenly lose their resistance to the flow of electricity on cooling. The phenomenon remained a laboratory curiosity until 1954 when G. B. Yntema at the University of Illinois, made the first successful superconducting magnet and even at that point magnet performance fell well below that predicted by the properties of the superconductor. The slow progress can be partially attributed to the difficulty in obtaining the extremely low temperatures required, and the lack of understanding of how to create electrically and thermally stable wires from superconductors. But the primary limitation was that the superconducting phenomenon was not only limited to low temperatures but also to a restricted range of electrical current density and magnetic field and that the range of these properties was particularly limited in early superconductors. The maximum values of temperature, electrical current and magnetic field are interdependent and when plotted in 3 axes form a "critical surface" (Fig. 1). Those early superconductors, such as Pb, In and Hg are classified as Type I superconductors, these are superconductors in which magnetic flux is excluded from their bulk and the critical current density is limited to a surface layer of approximately one tenth of a micron. The maximum fields in which these superconductors can operate are usually less that 0.1 T (similar to the flux-density between the poles of a horseshoe permanent magnet). These limitations make Type I superconductors impractical for wire and cable applications. All "technical superconductors," that is superconductors that can be readily fabricated into wires and cables for high current applications, are Type II superconductors. In Type II superconductors, magnetic flux penetrates the bulk of the superconductor to form individual flux quanta (***see Electrodynamics of Superconductors: Flux Properties - P. H. Kes)***. In the most widely used technical superconductors, Nb-Ti and Nb_3Sn, the upper critical fields are 13 T and 27 T respectively and current densities > 10^9 A/m² can be carried (compared to ~ 10^7 A/m² for domestic Cu wire). In Fig. 2 the critical current densities at 4.2 K are compared for strands or tapes that are fabricated in lengths of more than 100 m. The temperature range is still limited (the critical temperatures for Nb-Ti and Nb_3Sn are 10 K and 18 K respectively) but for many applications the cost of insulation and refrigeration is more than offset by the reduced energy costs resulting from non-resistive current flow. Because the amount of energy lost in current flow through a superconducting magnet is extremely low, it can be operated without a power supply once the magnet has been charged. This mode of operation, termed "persistent" is very desirable for MRI applications and NMR applications because the current flow (and consequently the field) is very stable. Liquid He is now readily available and provides cooling to 4.2 K at atmospheric pressure and as low as 1.8 K at reduced pressure.

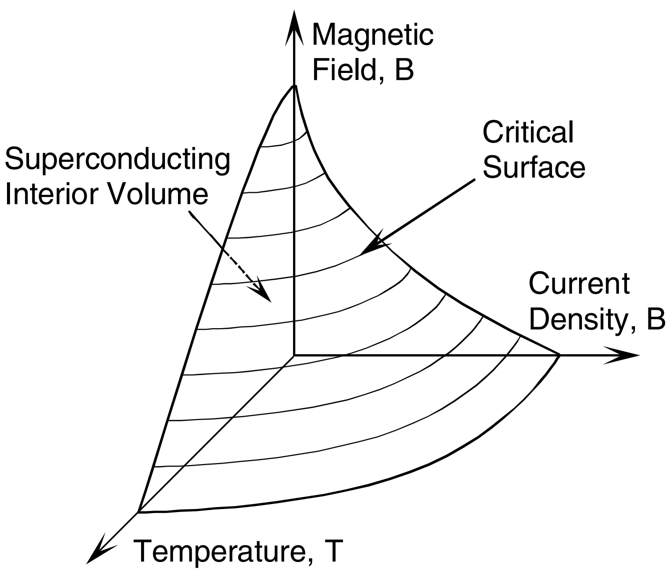

Figure 1. Schematic illustration of the critical surface for a Type II superconductor. The applied field (B), the temperature (T) and the current density (J) must be maintained below the critical surface in order to retain superconductivity.

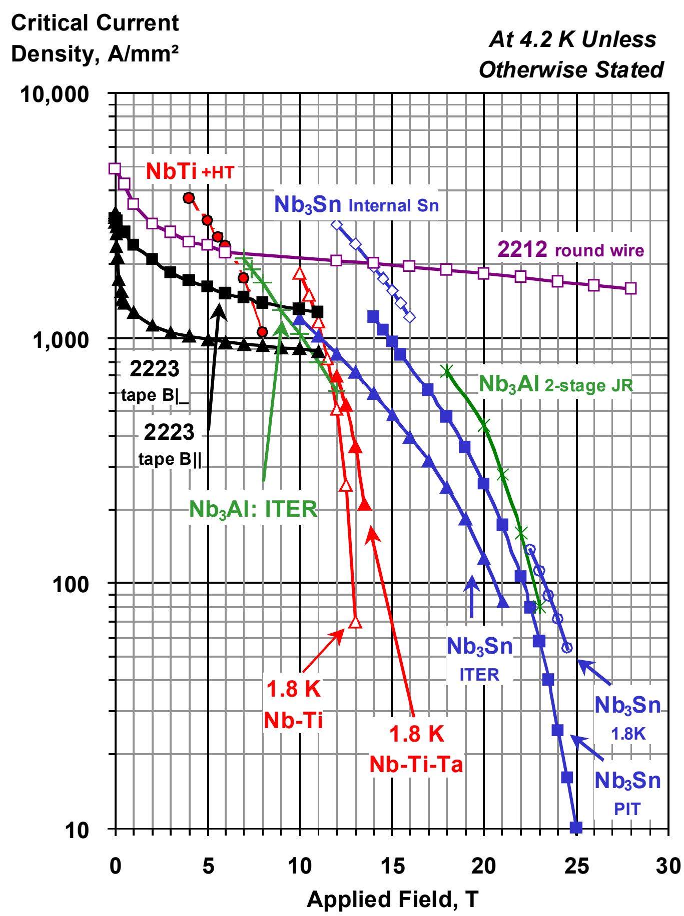

Figure 2. Comparison of critical current densities (at 4.2 K unless otherwise stated) available in strands and tapes of more than 100 m. (see http://www.asc.wisc.edu/plot/plot.htm for the most recent versions of this plot).

Recent advances in insulation and refrigeration technology have also made the application of superconductors more widespread. The discovery of HTS superconductors (ceramic superconductors with critical temperatures above the boiling point of liquid nitrogen (77 K) in 1986 (***see High-temperature Superconductors: Thin Films and Multilayers -- D. G. Schlom and J. Mannhart***) dramatically increased interest in the application of superconductivity and the discovery of superconductivity at 39 K in MgB_2 in 2001 further extended the temperature range for intermetallic superconductors.

Superconductors must be formed into composite wires in order for them to be used in high current applications and these wires may also be cabled. The wide variety of mechanical properties of superconductors - from strong ductile alloys like Nb-Ti to brittle ceramics such as HTS superconductors means that the wire processing routes vary greatly. Of the HTS superconductors only one, Bi-2212, is manufactured in round wire form, and HTS superconductors are more commonly manufactured as multifilamentary tapes. The brittle superconductors cannot undergo wire drawing and are consequently mechanically processed in the form of ductile precursors or fine powders that are reacted to form the superconductors at final size. For Nb-Ti, the alloy can be cold worked to a remarkable extent but heat treatments are also applied during processing in order to introduce a second phase into the microstructure that will ultimately pin the fluxoids in the final wire. Because of these variations the types of processing will be introduced separately and by superconducting material. There are, however, key components that are common to all superconducting strands.

2. General Strand Requirements

2.1 Matrix and Filaments

Superconducting wire is almost always of a multifilamentary design in which individual continuous filaments (< 30 μm in diameter) are embedded in a high conductivity matrix. When conditions in a localized region of a superconductor exceed the critical surface, that area will start to conduct resistively producing local heating. The resulting heat and current transfer will start a cascade effect and result in a rapid transition of the whole superconductor to the normal state. The ability to transfer heat and current away from localized regions by subdividing the filaments into a high conductivity matrix was a key step towards producing practical superconductors. The primary components of cryogenic stabilization were not formulated until the mid-1960s (see Stekly and Zar 1965). The most desirable matrices are Cu or Al but Ag is required for the processing of HTS superconductors where oxygen diffusion through the matrix is required during heat treatment. External stabilizer is often added after heat treatment, this is particularly the case for Al which has thermal and density advantages over Cu but is difficult to fabricate as the matrix of a composite wire. In addition to stability requirements, fine filaments also serve the purpose of limiting hysteretic loss, not only for ac applications but also for dc applications. The filament diameter requirements for ac applications are quite severe with desired filament diameters less the 1 μm. For ac applications a Cu-Ni matrix is often used to reduce proximity coupling of the filaments.

2.2 Filament Uniformity

As the critical current per unit cross-sectional area is limited by the material properties, the amount of current that can be carried by an individual filament is reduced if the filament is locally necked to a smaller diameter. Current may be locally transferred to adjacent filaments but there is a broadening of the critical current transition and a reduction in time that the strand may be operated in the persistent mode (crucial for MRI application). With final filament diameters of less that 20 microns often required, this imposes a very high level of quality control on the processing of the strands. The degree of filament uniformity is reflected in the sharpness of the superconducting transition with increasing current. In the early stages of the resistive transition, the curve of voltage, V against current, I, can be described by the power law:

$$V \propto I^{n} \qquad (1)$$

The value of n (the transition index) decreases with field and the more uniform the filament cross-sectional areas the more linear the decrease in n-value and the higher the initial low field value (see Warnes and Larbalestier 1986). An electric field, E, is generated along the superconductor carrying a current density, J, that is related to the critical current density of the superconductor, J_c at field E_c by the transition index, n:

$$E = E_c\,(J/J_c)^{n} \qquad (2)$$

For composites based on Nb-Ti strands the value of n (5 T) can be 50-100, in Nb_3Sn for NMR application the values are in the range of 40-80. The high n-values in Nb-Ti strands correspond to variations in filament cross-sectional area of less than 2% (coefficient of variation)[Lee and Larbalestier ASC92]. In HTS superconductors the range of available n-values is presently only 10-20 and persistent mode operation is not feasible under these conditions.

2.3 Critical Current Density and Flux Pinning

Pure annealed superconductors do not carry very much current because once current passes through the superconductor a Lorentz force is induced on the flux lines. When they move, the flux line lattice (FLL) dissipates energy and the superconductor eventually goes "normal" (***see Electrodynamics of Superconductors: Flux Properties - P. H. Kes and Superconducting Materials: Irradiation Effects W. K. Chu)***. The flux-lines, however, can be held in place by defects in the superconductor, a process termed "flux-pinning." In A15 based superconductors (such as Nb_3Sn) increasing the grain boundary density has been shown to increase critical current density (see Scanlan et al. 1975 and Ochiai et al. 1986). In Nb-Ti a linear increase in critical current density is observed with volume % of α-Ti precipitate (see Lee 1990). Consequently the introduction of pinning defects and the refinement of grain size are key elements to the success of technical superconductors.

2.4 Twisting

Twisting of the strand about its drawing axis is typically required to reduce flux-jump instability caused by varying external fields, and to reduce eddy-current losses. The twisting is ideally applied just before a multifilamentary strand has reached final size so that the twist can be locked into place by a further die-pass. The higher the expected rate of change of field, the tighter the required twist pitch. For the relatively steady-state dipole magnets for the Superconducting Super Collider, approximately 80 rotations along the drawing axis per meter were required, for ac application with a similarly sized strand the number of twists per meter might be 300. Typically twist pitches cannot be higher than 8 times the wire diameter, and normally a twist pitch of 10 to 20 times the diameter is used.

2.5 Final Shaping and Cladding

The final cross-section of the strand can be controlled by die shape and size or by using independently adjusted rollers operating along the strand surface. In this way square or rectangular cross-section filaments can be produced. Alternatively the strand can by inserted into a channel in a larger form, most commonly a rectangular Aluminum external stabilizer.

2.6 Cabling

Individual strands can be cabled or braided together to form a conductor with a higher current carrying capacity. The most common design for Nb-Ti magnets is the Rutherford cable, which consists of a fully transposed, flat cable. Using this approach, high aspect ratio cables can be produced with as many as 46 strands (see Scanlan et al. 1997). Strands may also be drawn into a larger conduit or combined with external stabilizers. A cross-section of a cable-in-conduit-conductor (CICC) is shown in Fig 3. As in the single strand-in-channel aluminum process multiple strands have been applied to surface channels in circular cross-section aluminum rods.

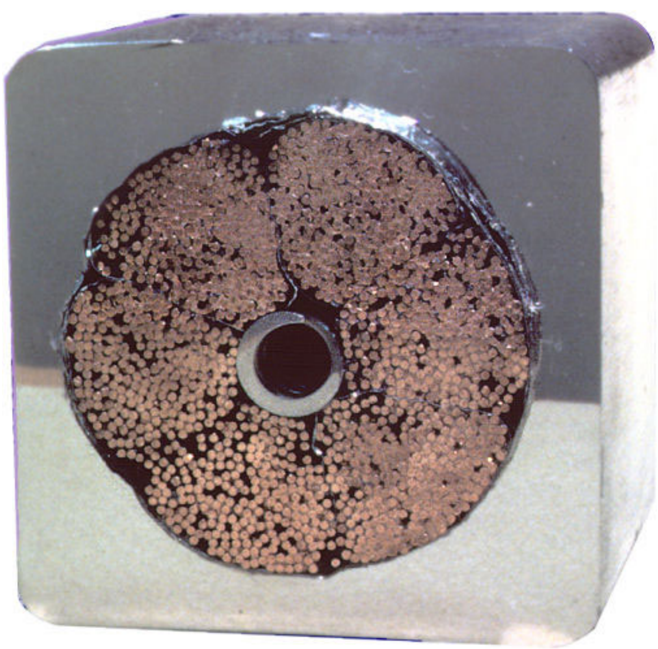

Figure 3. 3. Cross-section of cable-in-conduit-conductor (CICC). This 51 mm diameter Incoloy® jacketed cable contains 6 subcables; each containing 180 Nb_3Sn based superconducting strands.

2.7 Length Dependent Parameters

Both commercial Nb-Ti and Nb_3Sn strand are made in lengths of over a kilometer and variations can occur over the length of the strand because of the difference in mechanical properties of the components and because bonding of the monofilaments occurs during mechanical reduction rather than prior to it. In Nb-Ti variations in critical current, I_c, along the length of strands can be directly correlated with variations in Cu/Nb-Ti ratio along the length as shown by Kanithi et al 1990. In their study of strand developed for the Superconducting Supercollider project, they showed that the variation in I_c (due to variations in the intrinsic superconducting properties, the strand diameter and Cu/Nb-Ti ratio as well as measurement error) was more than twice the variation seen in J_c (due to just the intrinsic superconducting properties and measurement error). Because HTS based strands are still in their production infancy a different phenomenon is observed: As production length is increased, the overall I_c declines because it is very difficult to maintain the ideal conditions (grain alignment, heat treatment temperature, low porosity) necessary for good HTS strand over long lengths.

3. Superconducting Strand and Cable Manufacture by Material

3.1 Nb-Ti

3.1.1 Alloy Composition

Nb-Ti has become the dominant commercial superconductor because it can be economically manufactured in a strong and ductile form with both high current density and high resistive transition index. The starting point for fabrication of Nb-Ti strand is an alloy of between 46.5 and 50 wt.% Ti. Decreasing Ti over this range increases both the critical temperature, T_c,, and the upper critical field, H_{c2} (which at 4.2 K has a maximum value of 11.5 T at 44 weight % Ti). The increase in T_c and H_{c2}, however, is offset by a decrease in the amount of Ti available for precipitation of the α-Ti phase desired for flux-pinning and high critical density. The composition of the Nb-Ti also affects the precipitate morphology: if the α-Ti is formed at grain boundary intersections it tends to be uniform in size and distribution and does not significantly affect strand ductility, higher Ti compositions, however, also produce fine distributions of Widmanstätten-type precipitation in the grain interiors resulting in both a non-uniform microstructure and a significant hardening of the Nb-Ti. Because all these factors are sensitive to composition it is very important to start with a homogeneous alloy. With final filament diameters well below 0.05 mm the alloy must also be free of unmelted Nb or nonductile inclusions that may result in filament and ultimately strand breakage. Although the large difference in the melting points of Ti and Nb makes this a difficult alloy to manufacture, homogeneity levels in commercial Nb-47wt.%Ti alloys are now typically much better than ± 1.5 wt. % Ti. Impurity content has been traditionally kept low and consistent but recent work has shown that increasing the allowable content of iron can considerably refine the precipitate size without adversely affecting the precipitate volume (see Smathers et al 1996).

3.1.2 Extrusion and Billet Assembly

The as-cast Nb-Ti ingot is hot forged to the required diameter and then annealed in the single phase β region (approximately 2 hr at 870 °C). For fine filament Cu matrix composites the Nb-Ti ingot is then sealed inside a high purity Cu extrusion can, that is subsequently warm extruded to form a well bonded monofilament. Monofilament production billets ready for extrusion are shown in Fig. 4. Billet assembly is perfumed in a clean environment in order to avoid introducing particles that would not co-deform to the sub 0.05 mm filament size. Where high critical current densities and fine filaments are desired a Nb diffusion barrier is wrapped around the Nb-Ti rods in order to inhibit the formation of brittle Cu-Ti intermetallics during heat treatment (see Wilson 1972). The monofilament is then reduced in diameter by wire drawing, typically finishing with a hexagonal die to produce filaments that can be efficiently restacked. The thickness of the Cu around the Nb-Ti at this stage is important because it determines the spacing between Nb-Ti filaments when the Cu/Nb-Ti monofilaments are stacked together. For optimum mechanical stability in Nb-Ti/Cu multifilamentary composites, a filament spacing to filament diameter (s/d) ratio of 0.15 to 0.20 is ideal (see Gregory et al. 1987). Usually additional stabilizer is required and that may be added by increasing the wall thickness of the extrusion can or adding a central core of stabilizer core. For DC magnet application, it has been established by Ghosh et al (1987) that a minimum Cu thickness of 0.4 µm to 0.5 µm is required to reduce the magnetization associated with proximity filament coupling. For s/d

Figure 4. Monofilament Cu-clad Nb-Ti extrusion billets being inspected after welding. Image courtesy of Hem Kanithi, Outokumpu Advanced Superconductors Inc..

ratios of 0.15 to 0.20, the minimum Cu thickness requirement limits the minimum filament diameter to ~3 µm when using a pure Cu matrix. If smaller filaments are required, Ni or Mn can be added to the Cu between the filaments (see Hlasnik et al 1985, Cave et al 1989, Kreilick et al 1988).

The monofilament is then restacked inside another Cu extrusion can to form the final multifilamentary composite. The size of this extrusion can be up to 330 mm in diameter with a weight of 400 kg. As many as 4000 filaments may be assembled in one extrusion. Alternatively, large numbers of fine filaments can be produced by restacking a previously extruded multifilamentary billet, using this approach strands with up to 40,000 filaments have been manufactured. Where a small number of large filaments are desired (typically for low-field MRI application), Nb-Ti rods can be directly inserted into gun-drilled holes in a solid high purity Cu extrusion billet. Although warm extrusion helps bond the composite, as much of the subsequent processing as possible is performed cold by wire drawing because the cold work strain introduced into the Nb-Ti is an essential element in developing the high critical current microstructure.

3.1.3 Precipitation Heat Treatment

Precipitation heat treatments are applied after sufficient cold work has been applied following the multifilamentary extrusion. If too little cold work is applied before heat treatment, Widmanstätten precipitation will occur, causing increased hardness (reducing drawability) and producing a non-optimum precipitate size and distribution. Lee et al. (1989) found that the amount of prestrain required increases linearly with weight % Ti. Consequently a higher prestrain is required to suppress Widmanstätten in a chemically inhomogeneous alloy than would be required in a homogeneous alloy. For Nb-47wt% Ti, the required prestrain is ~5 but this rises steeply to 9 for a 55 wt% Ti alloy. Heat Treatments are typically at 375 ºC to 420 °C, ranging from 20 to 80 hrs in duration. Multiple heat treatment and drawing cycles are required to produce high critical current densities (see Li Cheng-ren, 1983). Whereas an initial heat treatment will only yield approximately 10 volume % precipitate, by applying additional cold work strain, the effect of the slow diffusion rate at these temperatures is again overcome and more precipitate is produced. Second and third heat treatments typically yield 15 and 20 volume % of alpha Ti precipitate respectively. The strain between heat treatments is 0.8 to 1.5 and at least three heat treatments are usually applied. A linear relationship between the optimized critical current density and the volume of precipitate Nb-47 weight % Ti alloys has been established by Lee et al. (1990). 20 % volume of α-Ti precipitate is sufficient to produce a critical current density of > 3000 A/mm² at 5 T, 4.2 K. Increasing Ti content increases the precipitation rate and amount but higher pre-strains are required if good ductility and long piece length is to be maintained. Alternatively the pinning sites can be introduced mechanically by hand-assembling the desired microstructure at large-size, in the same way as the multifilamentary billets are assembled, and then reducing the dimension to match the fluxoid spacing by multiple re-stacking and drawing cycles. This approach is called APC, for artificial pinning center. With

APC strand no additional heat treatment is necessary and a greater flexibility is possible in the microstructural components. Despite superior low field (< 5 T) performance, the APC approach has not reached commercialization because of the costs associated with the multiple re-stacking approach.

3.1.4 Final Wire Drawing

After final heat treatment the alpha-Ti precipitates are roughly equiaxed in transverse cross-section, 100 nm to 200 nm in diameter with an extension along the wire axis giving an aspect ratio of 5-20. The extensive final wire drawing (an engineering true strain of 5), however, produces a plain strain condition in the BCC β-Nb-Ti, which is supported by intercurling of the Nb-Ti grains. This results in distortion of the α-Ti precipitates into densely folded sheets during final wire drawing (see Fig 5.a). The folding process rapidly decreases the precipitate thickness and spacing with a dependence of $d^{1.6}$ (where d is the strand diameter) and increases the precipitate length per area with a dependence of $d^{-1.6}$, as measured by Meingast et al. (1989). The critical current density increases as the microstructure is refined until it reaches a peak, after which there is a steady decline. The peak in critical current density for a monofilament or a multifilamentary strand with uniform filaments occurs at a final strain of approximately 5. If the filaments are non-uniform in cross-section (sausaged) the peak occurs earlier and at a lower critical current density. A strand that has a premature (and lowered) peak in critical current density during final drawing is described as extrinsically limited because it has not attained the intrinsic critical current density of the microstructure. The most common source of extrinsic limitation is sausaging of the filaments due to intermetallic formation or lack of bonding between the components of the composite. High performance strand (as in Fig. 5b) has sausaging reduced to a very low level (a coefficient of variation for the filament cross-sectional areas of approximately 2 %). With tight quality control, uniform properties and piece lengths exceeding 10 km should be expected.

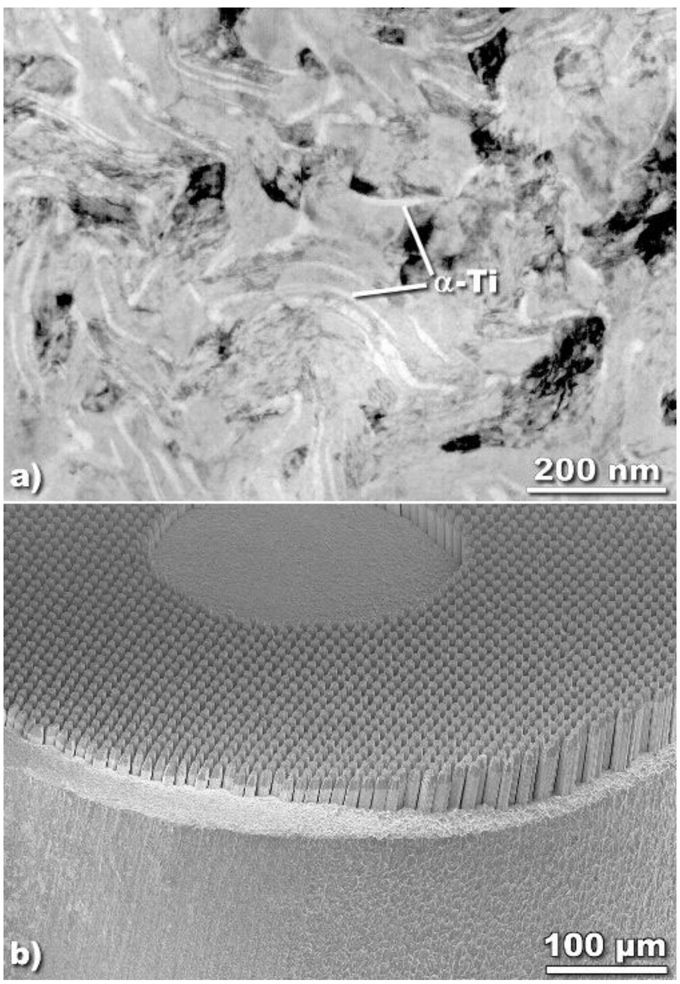

Figure 5. a) Transmission electron microscope image of high critical current density Nb-Ti microstructure with folded sheets of alpha-Ti precipitate. b) Etched cross-section of Nb-Ti based superconducting strand fabricated by IGC-AS (now Outokumpu Advanced Superconductors) for the Interaction Region Quadrapole Magnets of the Large Hadron Collider at CERN.

3.2 Nb_3Sn

Nb_3Sn is the second most widely use superconductor and has a higher upper critical temperature (18.2 K) than Nb-Ti. It is one of several A15 structure compounds that are superconducting. Other A15 superconductors or interest include Nb_3Al (T_c of 19.1 K) and Nb_3Ge (T_c of 23.2). Nb_3Al has been manufactured in long lengths and has a better strain tolerance than Nb_3Sn and better performance at very high field (>22 T) making it of importance to high field NMR inserts. But is much more complex and expensive to fabricate than Nb_3Sn because of the mechanical differences between Nb and Al and because the optimum Nb_3Al composition A15 can only be formed by high temperature processing (>1000 °C). Nb_3Sn, on the other hand, is widely manufactured and has shown sufficient strain tolerance in practice to be used successfully in very large solenoids such as the ITER CS model coil which stored 640 MJ of energy (see Kato et al. 2001) and high field (> 21 T) inserts for NMR application (see Kyoshi et al. 2001). Because A15 materials are brittle, all production routes use ductile precursors that are heat treated to form the A15 at final size by solid state diffusion. At an early stage it was found that the presence of Cu greatly aids the formation of Nb_3Sn at temperatures below 800 °C. It has also been found that adding Ti (0.7-1 wt. %) or Ta (7.5 wt%) improves the critical current density at high fields (> 12 T).

The three basic production routes currently used by commercial Nb_3Sn vendors, the bronze process, the internal Sn, and the powder in tube fabrication techniques, are illustrated in Fig. 6. The internal Sn process may use a jelly roll of Cu and Nb sheets, as illustrated in Fig. 6, or may use Nb (or Nb alloy) rods in a Cu matrix as shown in Fig. 7.

3.2.1 Bronze Process

For MRI application the most common route is the "bronze process" in which Nb alloy rods are first clad in high purity ductile Cu-Sn bronze and then assembled inside another Cu-Sn tube in a similar way to the production of Nb-Ti filaments in Cu for Nb-Ti strand. As with Nb-Ti multiple restacks can be used to increase the filament number. Under heat treatment (typically 650 °C to 725 0C) the Sn from the bronze reacts

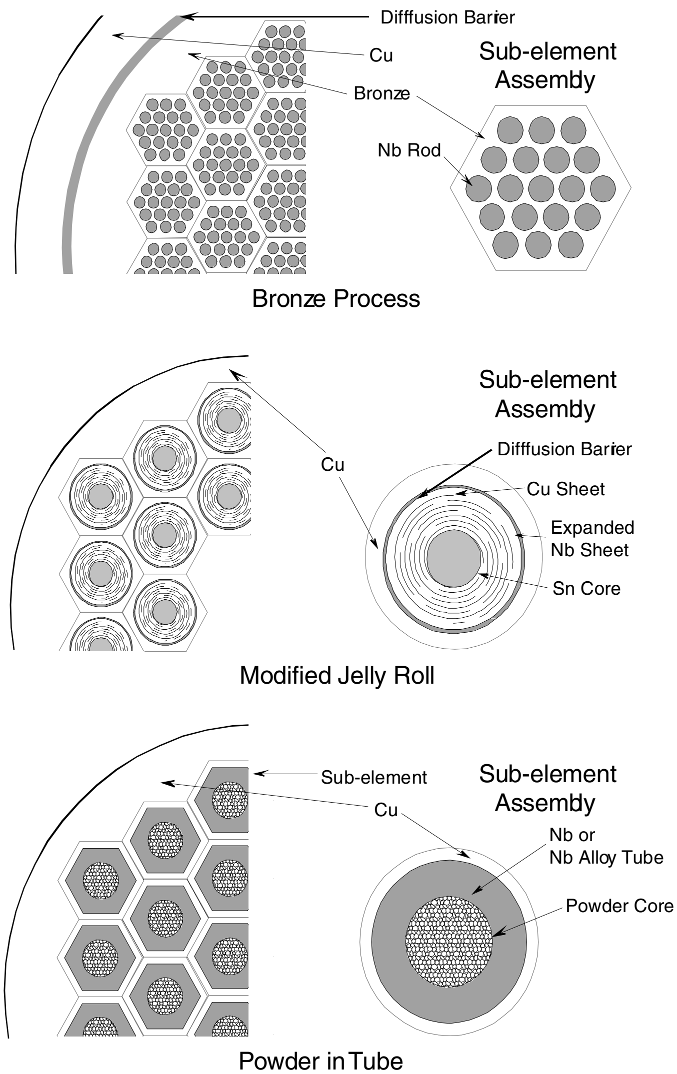

Figure 6. Schematic illustration comparing the bronze process, modified jelly roll (internal Sn), and powder in tube fabrication techniques for Nb_3Sn based superconducting strand.

with the Nb to from the superconducting A15 compound. As the Cu-Sn alloy does not act as a stabilizer, additional high purity Cu must be added outside, and/or inside the bronze-Nb filament composite, with a Ta and/or Nb diffusion barrier between to eliminate Sn contamination of the stabilizer. An example of a bronze-process strand is shown in Fig. 8. Vanadium has also been used as a barrier but results in a reduced critical current density. This process can yield a strand with a very high uniformity in filament size and distribution, which makes it an ideal product for high field NMR and other applications where a minimum of hysteresis loss is desired. The bronze, however, quickly work hardens during wire drawing and must be annealed frequently in order to maintain strand ductility, the extra processing steps significantly increasing the cost of the strand. The Sn content in the composite is also limited by the amount of Sn (<15 wt.% Sn) that can be added to bronze while maintaining ductility. The impact of insufficient Sn is most noticeable on critical current density. Recent development in the bronze process have centered on the use of specially processed high Sn bronzes (up to 16 wt. % Sn) that

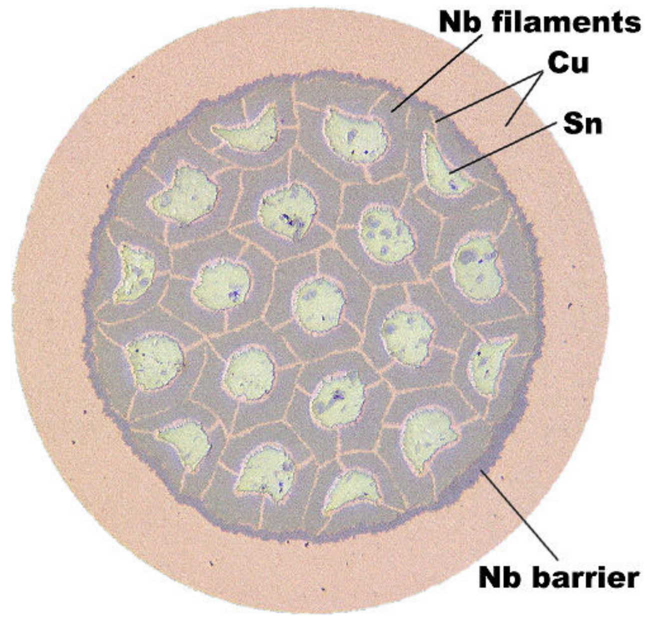

Figure 7. Transverse cross section of a rod-process internal Sn Nb_3Sn strand prior to diffusion heat treatment. This strand was designed for high critical current density by IGC-AS (now Outokumpu Advanced Superconductors).

have good ductility and high homogeneity (see Sakamoto et al. 2000).

3.2.2 Internal Sn Process

Higher Sn content and higher critical current density can be achieved by keeping the Sn separate from the Cu during strand fabrication. This is the basis for the internal Sn process which places and Sn core inside a Nb-filament/Cu matrix. The Sn core can be alloyed as a carrier for the Nb_3Sn allowing element or to improve the mechanical properties of the soft Sn. Strand based on this process has achieved the highest critical current densities for Nb_3Sn (in excess of 2400 A/mm² in the non-stabilizer package. The high critical current densities are achieved, in part, by reducing the amount of Cu in the Cu/filament/Sn package and the resulting reduction in filament coupling results in an undesirable increase in filament coupling. There are two distinct sub-categories of internal Sn process strand based on the form of the Nb filaments. In the "rod-in-tube" RIT process internal Sn the Nb filaments are assembled by inserting rods of Nb into pre-drilled holes in a Cu billet billet. The second internal Sn method is termed modified jelly roll (MJR) and used an expanded metal sheet of Nb co-wrapped with a Cu sheet to create the individual Nb filaments in a Cu matrix. Both of these techniques achieve very high current densities but limitations to the sizes of the billets (because of the restricted depth of the gun-drilled holes for rod-process and size limitations to deforming the MJR stacks) means that billet sizes are typically only 20 kg and processing costs are subsequently much higher than for Sn. As in the bronze process, the individual Cu-Nb-Sn sub-elements are clad in a diffusion barrier (Ta or Nb or TaNb alloy) to prevent poising of the Cu stabilizer by Sn diffusion. Sn diffuses rapidly through Cu at the temperatures used for the A15 forming heat treatment (up to 700 °C) and barrier integrity is consequently of great concern. The heat treatment of the strands

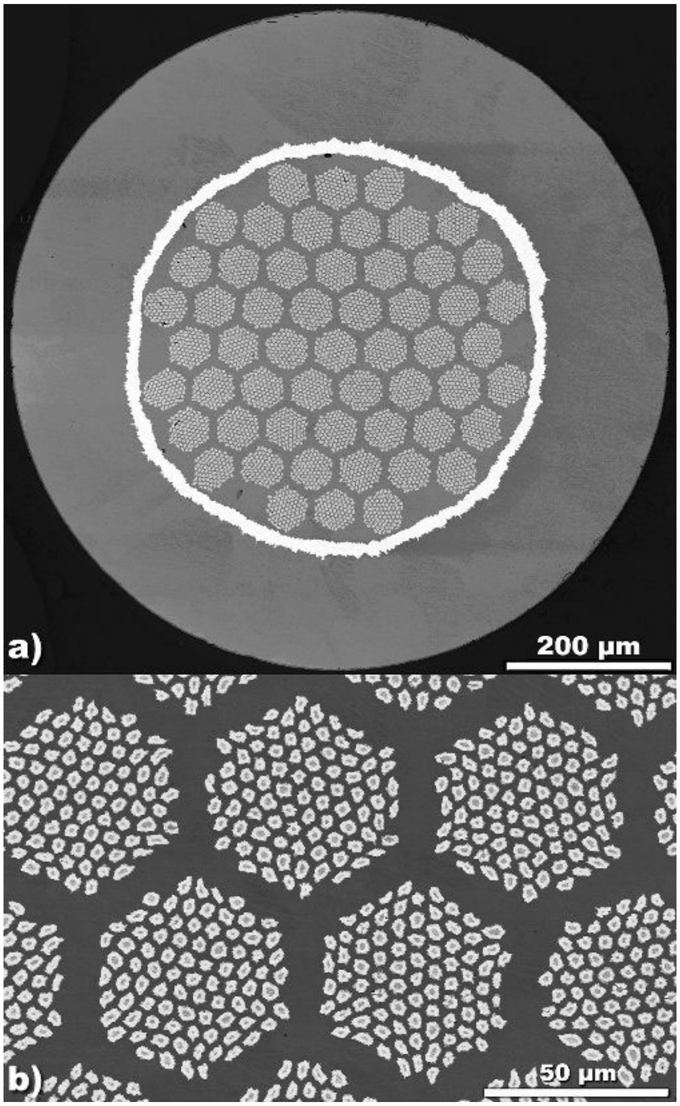

Figure 8. Bronze process Nb_3Sn strand fabricated by Vacuumschmelze for ITER shown in a) full cross-section and b) in filament detail. The filaments have a central unreacted core of Nb.

to form the A15 phase is preceded by multiple lower temperature steps designed to combine the Sn with the Cu without Sn melting. Both the RIT and MJR technique can also be used to fabricate precursor strand for Nb_3Al production.

3.2.3 PIT Process

Nb_3Sn may also be formed from higher Sn content Nb-Sn phases (Nb_6Sn_5 and $NbSn_2$) by inserting the intermetallics in powder form into tubes of Nb and reacting at 650 °C to 700 °C. The presence of Cu is also required to allow the formation of the A15 phases in the 650 °C to 700 °C temperature range in which fine grain size is maintained (see Lefranc and Muller, 1976). Elemental Sn is also added to improve the Sn to Nb ratio. No low temperature heat treatment is required for these strands and the A15 formation heat treatment takes a relatively short 50-75 hrs (180-270 ks). This process combines the best combination of high critical current densities (> 2200 A/mm² at 12 T and 4.2 K in the non-stabilizer volume) and low effective filament diameter (as low as 30 µm in high critical current density strand). The process is used to manufacture small quantities for demanding applications (see Lindenhovius, 2000) and has not received the cost benefits of commercial scale-up. The PIT technique can also be used for MgB_2, Bi-2223 and YBCO but porosity is an issue for these conductors when fabricated by this technique.

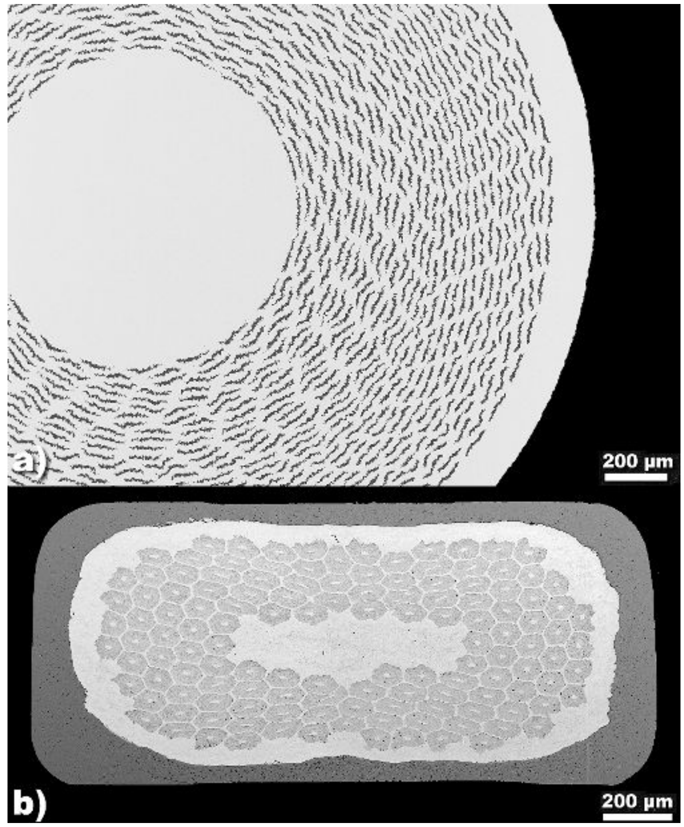

Figure 9. a) Precursor jelly-roll of Al and Nb fabricated by Oxford Advanced Superconductors. b) Multifilamentary Nb_3Al tape fabricated by the National Institute for Materials Science in Japan from a rapidly heated and cooled composite of jelly-roll precursors (fabricated by Hitachi Wire and Cable).

3.3 Nb_3Al

Nb_3Al has not achieved commercial strand status but it can be described as a technical superconductor because it can and has been fabricated into high performance and uniform km lengths that have been fabricated into full-scale devices. At magnetic fields above 20 T critical current densities can be obtained that are comparable to the best Nb_3Sn strands and useful critical current densities (>100 A/mm² non-stabilizer) can be achieved above 24 T. Perhaps the most important feature of Nb_3Al is the high strain tolerance of the Nb_3Al strands compared to Nb_3Sn. One ton (total length of 210 km) of mass-produced "jelly-roll" process strand (Yamada et al. 1994) was manufactured for the 13 T-46 kA Nb_3Al insert for the ITER Central Solenoid model coil. The "jelly-roll" of Nb and Al is created by co-winding sheets of Nb and Al together on an oxygen-free pure copper core. This will eventually become an individual filament in the final multi-filamentary strand. The assembled jelly-roll and core are inserted into an oxygen-free pure copper tube to create an extrusion billet. After hydrostatic extrusion the billet is drawn down to a small enough size that it can be restacked to create a multifilamentary billet. Again the billet was hydrostatically extruded and drawn, this time to the desired strand diameter size. The extrusion and restack process reduces the thickness of the Nb–Al layers in the filaments to less than one micron. The production yield rate for the ITER insert strand was 70% for strands longer than 1.5 km. The final strand is heat treated (800°C for 10 hrs is typical) to produce Nb_3Al. The critical current densities obtained by this technique are approximately 600 A/mm² at 12 T and 4.2K (Hosono et al 2002).

The highest upper critical fields and critical temperatures for Nb_3Al are based around high temperature heat treatments and rapid cooling. In the RHQT (Iijima et al., 1997) process Nb/Al composites (modified jelly roll, MJR or rod in tube, RIT) are resistance heated to 1900-2000 °C and then rapidly quenched into a molten Ga bath at 40-50 °C producing a metastable bcc supersaturated solid solution, $Nb(Al)_{ss}$, inside a Nb matrix. The heating time is ~ 0.1 sec. The $Nb(Al)_{ss}$ has excellent ductility and the strand can consequently be mechanically clad or cabled with Cu at this stage and the stabilized strand may also be wound into device form. The $Nb(Al)_{ss}$ is then transformed to Nb_3Al at 800 °C. Both the critical temperature, T_c, of ~17.8 K and the critical magnetic field, B_{c2}, of ~ 26 T are 0.7 K and 4 T lower for RHQT composites than the highest values obtained by laser or electron beam irradiation processed Nb_3Al (Takeuchi et al., 2000) and this difference has been attributed (Kikuchi et al., 2001) to stacking faults formed in the A15 phase. Two successful modifications to the basic RQHT technique specifically address the stacking fault issue: In the double rapidly-heating/quenching, DRHQ, technique the standard RQHT process is followed but instead of a conventional low temperature (<1000 °C) transformation heat treatment a second RQH process produces the A15 phase and this is followed by a long range ordering heat treatment at 800 °C for ~12 hrs (Kikuchi et al., 2001). The T_c for these stacking fault free strands has been measured at 18.4 K, which suggests very good stoichiometry; further more a critical current density of 135 A/mm² was obtained at 25 T (Kikuchi et al., 2002). A disadvantage of this technique is that the brittle A15 phase is formed during high temperature processing. Alternatively the TRUQ technique (TRansformation-heat-based Up Quenching) follows the initial RQH of the RQHT process with a short heating step to 1000 °C, at 1000°C the heat released by local transformation from the $Nb(Al)_{ss}$ to the A15 phase produces a rapid local heating and propagation of the reaction along the length of the strand. As the self heating is localized to the A15 volume the heat is quickly dissipated after reaction across the Nb and stabilizer volumes so that external Cu stabilizer applied after the initial RQH process is not melted. A further anneal at ~800 °C then provides long range ordering to the A15 phase (Takeuchi et al., 2000).

3.4 HTS Superconductors

HTS superconductors have demanded great interest because of their ability to superconduct with relatively inexpensive liquid nitrogen cooling and their impressive high field performance. HTS wire and tapes have not achieved the same commercial impact as LTS strands, however, because of the relative difficulty of producing long low cost lengths of conductor. The primary sources of this difficulty are the anisotropy in their superconducting behavior and the barrier to current flow presented by high angle grain boundaries in these materials. Consequently the strands must be fabricated with a remarkable degree of grain alignment. Further complicating the process is a high sensitivity to heat treatment temperature (<1 °C control must be exerted for across the entire strand length for Bi-2212) and a need for oxygen diffusion into the HTS composite during fabrication. This second requirement effectively means that silver must be used the superconducting strand stabilizer. Of the HTS superconductors only Bi-2212 can be readily made into round-wire form strand. All the other HTS superconductors require a tape format. $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ based conductor has been shown to be capable of application to superconducting power cables, magnetic energy-storage devices, transformers, fault current limiters and motors but widespread application will require significant cost reduction in processing. YBCO based superconductors have the highest recorded critical current densities but at present there is no viable wire production technique available for YBCO and critical current densities fall rapidly with superconductor thickness above 0.5 μm and with length beyond 1 μm.

3.4.1 Bi-2223

$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ ("Bi2223") is most readily fabricated using powder-in-tube techniques very similar to those used for Nb_3Sn, with Ag replacing the Cu tubes used for Nb_3Sn. In addition to standard wire drawing techniques, groove rolling is also incorporated to bring powder filled monofilaments to restack size. Hot extrusion can then be used to bond the multifilamentary composite while increasing the powder density and reducing the billet diameter. Extrusion is followed by further drawing and groove rolling and finally rolling into tape. As a conventionally mechanically processed material this is readily scalable to large production quantities. The key issue is to increase the connectivity between the grains of the conductor. The prospect of two- to fivefold improvements in the performance of the present process, coupled to cost reductions triggered by significant scale-up and alternative routes such as overpressure processing (see Rikel et al., 2001) or melt processing (see Flükiger et al., 2001) could accelerate the early penetration of superconducting technology into the utility network.

Demonstration HTS transmission cable projects have utilized Bi2223 strand including test installations at Detroit Edison and Southwire in the USA. For the Detroit-Edison project a conductor was fabricated by American Superconductor that used four layers of Ag-sheathed Bi2223 tapes (29 km in total), each tape having an average critical current of approximately 118 A dc at 77 K. The tapes utilized oxide-dispersion-strengthened silver matrices as well as stainless steel reinforcement added to both sides of the HTS tape (Masur et al. 2001). For the Southwire project 30 m cables were produced from PIT B-2223 tapes manufactured by IGC. The measured critical current for the cables was 2980 A at 77 K (Sinha et al. 2001).

3.5 MgB_2

MgB_2 was discovered in early 2001 and has generated much interest as it has the highest T_c (39 K) of any intermetallic superconductor and has the lowest cost components. Like Bi2223, MgB_2 wires or tapes can use essentially the same technology as that used for Nb_3Sn powder-in-tube composites. Powder in tube offers a scaleable technology for future production of kilometer-length MgB_2 and has already been exploited for strand fabrication (see Jin et al., 2001 and Grasso et al., 2001). The perpendicular irreversibility field is less than for Nb_3Sn, the most widely used intermetallic superconductor, and this may restrict MgB_2 to applications of lower field.

4. Summary

Nb-Ti and Nb_3Sn superconductors are well established as commercial superconductors with stable markets for NMR and MRI devices as well as high magnetic field testing equipment. Future markets in fusion reactors, accelerator magnets and energy storage drive further developments. The strain tolerance of Nb_3Al should maintain interest in this material for high field applications where conductor cost is not as issue. The ability to use liquid Nitrogen as a coolant for HTS conductors, such as Bi2223, is important for applications such as power transmission lines which are not well suited for low temperature refrigeration. Further performance improvement and cost reduction will be required before HTS strands are economically viable. MgB_2 offers the potential of a low cost superconductor for the future that, while not being able to use liquid nitrogen cooling, is still able to benefit from reduced refrigeration costs due to its high T_c.

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