Chapter 9
Multifilamentary Superconducting Composites

Certain materials lose all resistance to the flow of electricity when cooled to within a few degrees of absolute zero. The phenomenon is called *superconductivity*, and the materials exhibiting this phenomenon are called *superconductors*. Superconductors can carry a high current density without any electrical resistance; thus, they can generate the very high magnetic fields that are desirable in many applications: magnetic resonance imaging, high-energy physics, and fusion energy programs. Other fields of application include magnetic levitation vehicles, magneto hydrodynamic generators, rotating machines, and magnets in general. Kamerlingh Onnes discovered the phenomenon of superconductivity in mercury in 1911. Since then, some 27 elements and hundreds of solid solutions or compounds have been discovered that show this phenomenon of total disappearance of electrical resistance below a critical temperature, T_c. Figure 9.1 shows the variation of electrical resistivity with temperature of a normal metal and that of a superconducting material, Nb_3Sn. The critical temperature is a characteristic constant of each material. Kunzler et al. (1961) discovered the high critical field capability of Nb_3Sn and thus opened up the field of practical, high-field superconducting magnets. It turns out that most of the superconductors came into the realm of economic viability when techniques were developed to put the superconducting species in the form of ultrathin filaments in a copper matrix as described below. A similar development route is used for the newer oxide superconductors.

Multifilamentary composite superconductors started becoming available in the 1970s. These are niobium-based (Nb–Ti and Nb_3Sn) superconductors, also referred to as *conventional* superconductors. The erstwhile record of critical temperature at which a conventional material became a superconductor was 23 K and was set in 1974. These conventional superconductors require liquid helium as a coolant, which is expensive. In 1986, there began a new era in the field of superconductivity, called high-temperature superconductivity (HTS), which started with the now well-known work of Bednorz and Muller. They reported of superconductivity at 30 K

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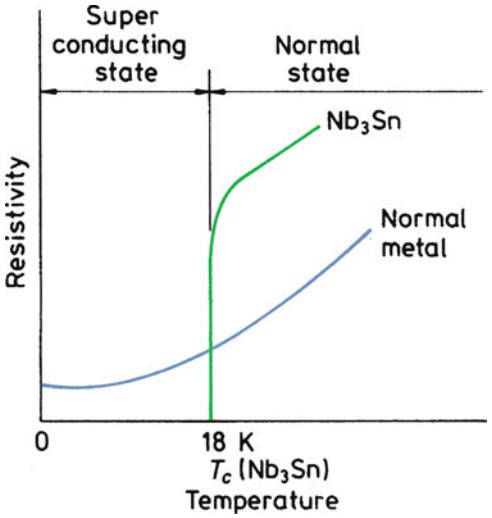

Fig. 9.1 Variation of electrical resistivity with temperature for a normal metal and a superconducting material, Nb_3Sn

in a ceramic containing lanthanum, copper, oxygen, and barium. This original discovery, for which Bednorz and Muller received a Nobel prize, set off a storm of activity. In 1987, Chu and Wu found a related oxide superconductor with a critical temperature above 77 K, the boiling point of liquid nitrogen. This had the chemical composition of $YBa_2Cu_3O_{7-x}$, and is commonly referred to as the *1-2-3 superconductor* because of the Y:Ba:Cu ratio. Since then other ceramic compounds with critical temperatures above 77 K have been discovered.

The oxide superconductors have the great advantage of having a T_c around 90 K, i.e., above the liquid nitrogen temperature (77 K). Thus, potentially, liquid nitrogen, a cheap and easily available cooling medium, could replace liquid helium, which is expensive and limited in supply. There are, however, many problems with these superconductors. These new ceramic superconductors have a layered, perovskite body-centered tetragonal structure and, not surprisingly, are very brittle. This problem of brittleness, as was pointed out in 1987 by some researchers including this author, makes it very difficult to make thin filaments of these oxide superconductors for use in, for example, magnet windings. Besides the inherent brittleness of ceramics, these superconductors carry very low current densities. It is true that the electrical resistance goes to zero around 90 K, but the troublesome fact is that these materials lose their superconductivity at very modest current densities, of the order of a few hundred A/cm^2. This has been attributed to impurities, misaligned grains, and the like. It turns out that the layered perovskite cuprates are all anisotropic, difficult to prepare in desirable shapes such as long continuous wires, and very poor at carrying current. In particular, the grain boundaries in a polycrystalline sample block the current. This is attributed to the extremely short (a few nm) coherence length in these oxides (Larbalestier 1996). Coherence length is a term that is related to the Fermi velocity for the material and the energy gap associated with the condensation to the superconducting state. A transition from the superconducting state to a normal state will have a transition layer of finite thickness which is related to the coherence length. Yet another problem is that the

performance of these oxide superconductors deteriorates drastically as the applied magnetic field increases. At a magnetic field of 1 T, the critical current density, J_c, is about 1–10 A/cm^2. For any reasonable commercial application, one needs a J_c of about 10^5 A/cm^2. The critical current density, J_c, is a function of the processing and, consequently, of the microstructure of the superconductor. This is where some innovative processing can be of great value. Heine et al. (1989) took just such a step when they partially melted Bi–Sr–Ca–Cu–O (BSCCO) in a silver sheath and observed that the resultant superconductor showed high J_c in the grains. There remains a large gap to be bridged between producing a small sample for testing in the laboratory and making a viable commercial product. We need superconductors (Larbalestier 1996) that "... must be electrically continuous, otherwise there can be no applications." They must also be strong and tough, amenable to being economically made into long lengths, and possess high overall J_c values. The term *overall* implies that all of the space required to make the superconductor must be taken into account when critical current density is computed (Larbalestier 1996). It should be pointed out that the Nb–Ti system took 15–20 years between its discovery and commercial availability. The new high-temperature oxide superconductors hold great promise, and it would appear that eventually some kind of composite superconductors will be used commercially as are the Nb-based conventional superconductors. Thus, it is quite instructive to review the composite material aspects of niobium-based superconductors, which we do first in this chapter. We describe the processing, structure, and properties of the conventional and high-T_c superconductors. Both are truly multifilamentary metal matrix composites. But first let us describe why we need these superconductors in the form of multifilamentary metal matrix composites.

9.1 The Problem of Flux Pinning

For a variety of applications, we need long-length superconductors of uniform properties, for example, large solenoids and coils for rotating machinery and magnets for plasma confinement in a fusion reactor. In conventional superconductors, ultrathin superconducting filaments are incorporated in a copper matrix to form a filamentary fibrous composite. In the high-T_c superconductors, we have ceramic superconducting material in the form of thin filaments in a metal matrix. Small diameter, continuous, superconducting filaments distributed in a high conductivity (electrical and thermal) matrix constitute nothing but a superconducting metal matrix composite (MMC). The main reason for using superconductors in the form of filamentary composites is that flux jumps can be avoided if the diameter of superconducting filaments is below a certain value (Irie 1994). It is important to realize that stable, superconducting magnets need flexible and continuous wires that can be wound; this became possible only after wires and cables were made of such MMC composites.

Superconducting filaments have a micrometer-size diameter that helps to reduce the risk of flux jump in any given filament. If a superconductor is perturbed, say, by motion or a change in the applied field, it leads to a rearrangement of magnetic flux

lines in the superconductor. This phenomenon is called *flux motion* and is an energy-dissipative or heat-producing process. When a current density J flows in a superconductor in the presence of a magnetic field, B, it experiences a Lorentz force per unit volume F_L, given by the cross product of J and B:

$$F_L = J \times B.$$

The Lorentz force acts in a direction perpendicular to both J and B. This force can result in motion of flux lines. Whenever the flux lines move (no matter what the source of this motion), they produce resistance. Hence, we need to pin the flux lines in a superconductor, which is done by appropriate microstructural control. The critical current density, J_c, corresponds to the Lorentz force that unpins the flux lines and makes them move. Thus, the pinning force is equal to $J_c \times B$. Any heat generated by flux motion will result in a temperature increase, which in turn will lead to a reduced critical current and more flux motion will result. The net result is that the superconductor is heated above T_c and reverts to the normal state. A practical solution to this problem is to make the superconductor in the form of ultrathin filaments so that the amount of energy (heat) dissipated by flux motion is too small to cause this runaway behavior; see Fig. 9.2. The high-purity copper or some other metal matrix provides a high-conductivity alternate path for the current. In the case of a *quench*, that is, superconductor reverting to the normal state, the metal matrix carries the current without getting excessively hot. The superconductor is cooled again below its T_c and carries the electric current again. This is the so-called *cryogenic stability* or *cryostabilization* design concept; namely, the superconductor is embedded in a large volume of low-resistivity metal and a coolant (liquid helium or liquid nitrogen) is in intimate contact with all windings.

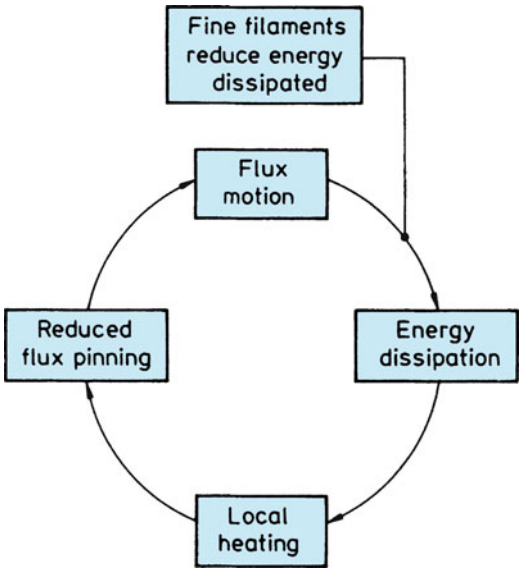

Fig. 9.2 Flux movement in a superconductor is caused by any change in current or field

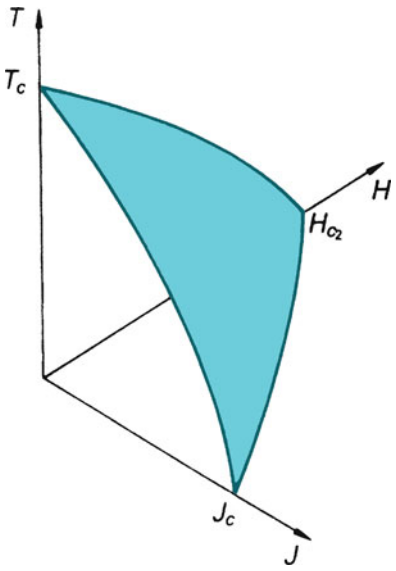

Fig. 9.3 The state of superconductivity in a material is described by three critical parameters: magnetic field (H), temperature (T), and current density (J). The material will remain in a superconducting state as long as it is below the shaded portion

9.2 Types of Superconductor

The technologically most important property of a superconductor is its capacity to carry an electric current without normal I^2R losses up to a critical current density, J_c. I^2R losses are known as Joule heating, with I and R representing the electric current and resistance, respectively. The critical current density, J_c, is a function of the applied field and temperature. The commercially available superconductors in the 1980s could demonstrate critical current densities of $J_c > 10^6$ A/cm^2 at 4.2 K, the liquid helium temperature, and an applied field of 5 T.

There are three parameters that limit the properties of a superconductor, namely, the critical temperature (T_c), the critical electrical current density (J_c), and the critical magnetic field (H_c); see Fig. 9.3. As long as the material stays below the shaded area indicated in Fig. 9.3, it will behave as a superconductor.

There are two types of superconductor:

Type I: These are characterized by low T_c values, and they lose their superconductivity abruptly at H_c.

Type II: These behave as diamagnetic materials up to a field H_{c1}. Above this field, the magnetic field penetrates gradually into the material, and concomitantly the superconductivity is gradually lost, until at the critical magnetic field H_{c2} the material reverts to the normal state.

All major applications of superconductivity involve the use of these type II superconductors. The magnetic field penetrates a type II superconductor in the

form of thin filaments called *magnetic vortices*, which are fixed by what are called *pinning centers*. When an electric current is applied, the Lorentz force exerted by current tends to move these vortices. If there is no pinning or if the pinning is weak such that the Lorentz force moves the vortices, then the motion of these vortices generates voltage and the resultant heat will destroy the superconducting state. An interesting demonstration of such a dynamic interaction of vortices with pinning centers was done by Matsuda et al. (1996) by means of a technique called *Lorentz microscopy*. They studied a niobium film sample in which they had made a square lattice of defects by ion irradiation. The sample was placed in a low-temperature specimen stage of a 300 kV field emission transmission electron microscope. The objective lens of TEM was replaced by an intermediate lens to make an out-of-focus image (i.e., a Lorentz micrograph) in which vortices appear as dark spots. One needs microstructural pinning of these flux lines in a filamentary superconductor embedded in a metal matrix.

In the following sections, we describe processing, microstructure, and properties of some important superconducting composite systems. Finally, we provide a summary of their applications.

9.3 Processing and Structure of Multifilamentary Superconductors

There are three main categories of multifilamentary superconductors: Nb–Ti-based ductile alloy superconductors, Nb_3Sn-type brittle superconductors, and ceramic oxide brittle superconductors.

9.3.1 Niobium–Titanium Alloys

Niobium–titanium alloys provide a good combination of superconducting and mechanical properties. A range of compositions is available commercially: Nb–44 % Ti, Nb–46.5 % Ti, and Nb–50 % Ti (all atomic percents).

In all these alloys, a $J_c > 10^6$ A/cm^2 at 4.2 K and an applied field of 7 T can be obtained by a suitable combination of mechanical working and annealing treatments. Strong flux pinning and therefore high J_c are obtained in these alloys by means of dislocation of cell walls and precipitates. The flux pinning by precipitates becomes important in high-Ti alloys because the Nb–Ti phase diagram indicates precipitation of α-Ti in these alloys; see Fig. 9.4. As pointed out earlier, the condition of stability against flux motion requires that the superconductor be manufactured in the form of a composite system: extremely fine superconducting filaments embedded in a copper matrix provide flux stability and reduced losses caused by varying magnetic fields. Fortunately, Nb–Ti and copper are compatible,

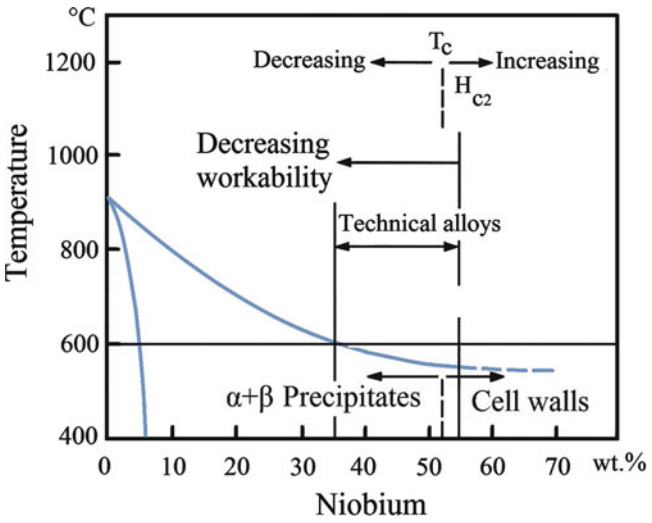

Fig. 9.4 Nb–Ti phase diagram showing the range of compositions used to make Nb–Ti superconductors [after Hillmann (1981)]

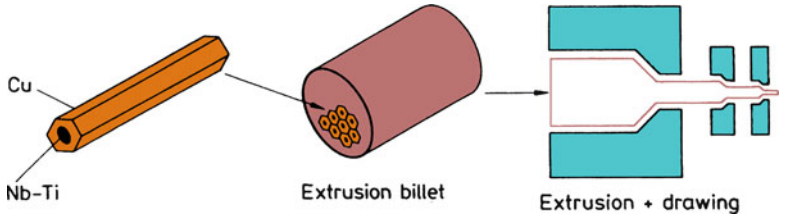

Fig. 9.5 Fabrication route for Nb–Ti/Cu composite superconductors

chemically and otherwise, and amenable to making filamentary composites. Figure 9.5 shows the essential steps in the fabrication of Nb–Ti composite superconductors. Annealed Nb–Ti rods are inserted into hexagonal-shaped high-purity copper tubes. These rods are next loaded into an extrusion billet of copper, evacuated, sealed, and extruded. The extruded rods are cold drawn to an intermediate size and annealed to provide the necessary dislocation cell walls and precipitates for flux pinning. This is followed by more cold drawing passes to the appropriate final size and a final anneal to get back the high conductivity of the copper matrix. Consider the specific case of Nb–50 % Ti alloy. Its initial microstructure consists of a β solid solution. The necessary cell structure and dislocation density for flux pinning purposes depend on the purity of the alloy and the size and distribution of the

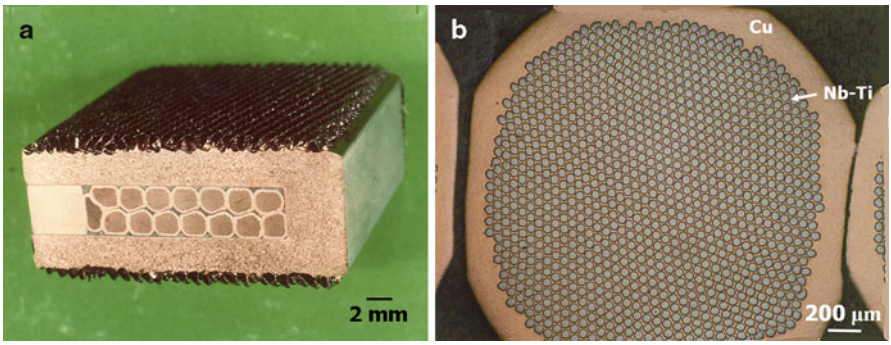

Fig. 9.6 (**a**) Compacted strand cable superconductor made from 15 multifilamentary strands each of diameter = 2.3 mm. (**b**) Magnified picture of one of the strands in (**a**) containing 1,060 filaments (diameter = 50 μm) (courtesy of Hitachi Cable Co.)

α particles after precipitation heat treatment. The α phase is nonsuperconducting; its main function is to aid dislocation cell structure formation. Dislocations and α particles are responsible for flux pinning and thus contribute to high J_c values. The amount and distribution of α particles depend on the alloy chemical composition, processing, and annealing temperature and time. For a Nb–50 % Ti alloy, a heat treatment of 48 h at 375 °C is generally used and results in about 11 % of α particles. A greater amount of α will reduce the ductility of the alloy. Higher annealing temperatures result in excessive softening, fewer dislocations, and lower J_c. The precipitation treatment is generally followed by some cold working to refine the microstructure and obtain a high J_c. The precise amount of strain given in this last step is a function of the superconductor design, that is, the distribution of Nb–Ti filaments and the ratio of Nb–Ti/Cu in the cross section.

The interfacial bonding is essentially mechanical. However, undesirable intermetallic compounds can form from any scratches on the surface of NbTi rod (Hillmann 1981). A hard ball of oxidized NbTi, about 1 μm in diameter, can form at a scratch on the surface of a NbTi rod. During extrusion, there is a snowball-like effect causing mechanical alloying and formation of a NbTi + Cu mixture. During subsequent annealing treatment, this mixture can turn into $(NbTi)Cu_2$ and/or $(NbTi)_2Cu$ intermetallic compounds. These brittle compounds can eventually easily crack and cause rupture of the superconducting filament.

Figure 9.6a shows a compacted strand cable-type superconductor made from 15 fine multifilamentary strands (strand diameter = 2.3 mm). Each strand in this figure consists of 1,060 filaments of Nb–Ti (diameter = 50 μm) embedded in a copper matrix. A magnified picture of one of the strands is shown in Fig. 9.6b, while a scanning electron microscope picture is shown in Fig. 9.7. The Cu–Ni layers seen in Fig. 9.7 provide the low-conductivity barriers to prevent eddy current losses in alternating fields.

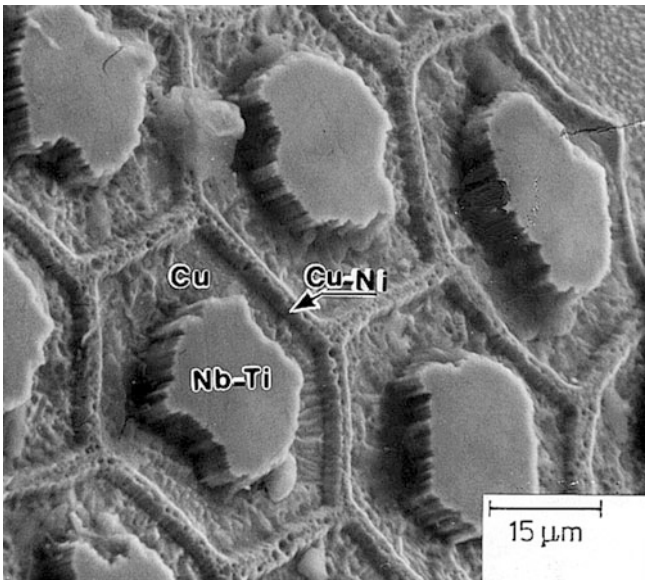

Fig. 9.7 Scanning electron microscope picture of Nb–Ti/Cu superconductor

9.3.2 A15 Superconductors

For applications involving fields greater than 12 T and temperatures higher than 4.2 K, the ordered intermetallic compounds having an A15 crystal structure (Nb_3Sn, V_3Ga) are better suited than the Nb–Ti type. The A15 compounds have the chemical formula A_3B, where A is a transition element and B can be either a transition or a nontransition element. In particular, Nb_3Sn has a T_c of 18 K. The higher the T_c, the lower the refrigeration costs will be and hence the tremendous interest in high T_c oxide superconductors. Superconducting magnets form an integral part of any thermonuclear fusion reactor for producing plasma-confining magnetic fields (see problem 9.6). Nb_3Sn is the most widely used superconductor for high fields and high temperatures. A characteristic feature of these intermetallic compounds having an A15 crystal structure is their extreme brittleness (typically, a strain-to-fracture of 0.2 % with no plasticity). Compare this to Nb–Ti, which can be cold worked to a reduction in area over 90 %. Initially, the compound Nb_3Sn was made in the form of wires or ribbons either by diffusion of tin into niobium substrate in the form of a ribbon or by chemical vapor deposition. V_3Ga on a vanadium ribbon was also produced in this manner. The main disadvantages of these ribbon-type superconductors were: (1) flux instabilities due to one wide dimension in the ribbon geometry, and (2) limited flexibility in the ribbon width direction. Later, with the realization that flux stability could be obtained by the superconductors in the form of extremely fine filaments, the filamentary composite approach to A-15 superconductor fabrication was adopted. This breakthrough

involving the composite route came through early in the 1970s. Tachikawa (1970) showed that V_3Ga could be produced on vanadium filaments via a Cu–Ga matrix, while Kaufmann and Pickett (1970) demonstrated that Nb_3Sn could be obtained on niobium filaments from a bronze (Cu–Sn) matrix.

The process of producing Nb_3Sn is shown schematically in Fig. 9.8. Sometimes, this process is referred to as the *bronze route*; the reason for this name will become clear presently. Niobium rods are inserted into a bronze (Cu–13 wt.% Sn) extrusion billet. This billet is sealed and extruded into rods. This is called the *first-stage extrusion*. The rods obtained after the first-stage extrusion are loaded into a copper can that has a tantalum or niobium barrier layer and extruded again, the *second-stage* extrusion. The second-stage extruded composite is cold drawn and formed into a cable, clad with more copper and compacted to form a monolithic conductor. This is finally given a heat treatment to drive Sn from bronze and convert the very fine niobium filaments into Nb_3Sn. A similar process can be used to make a V_3Ga superconductor, but it is not available commercially. Specifically, for the Nb_3Sn superconductors, the ratio of cross-sectional area of bronze matrix to that of niobium, called R ratio (= Cu–Sn/Nb), is an important design parameter that strongly affects the J_c value. It is important that a right amount of tin be available to form the stoichiometric Nb_3Sn phase. Too much of the bronze matrix will reduce the J_c value.

Thus, one uses a bronze with about 13 wt.% tin, the limit of solubility of tin in copper, which yields enough tin without affecting the formability. Arriving at an optimum value of the ratio R is critical because the resultant Nb_3Sn must be stoichiometric. One ensures this by using a high ratio of R (>3) and sufficiently

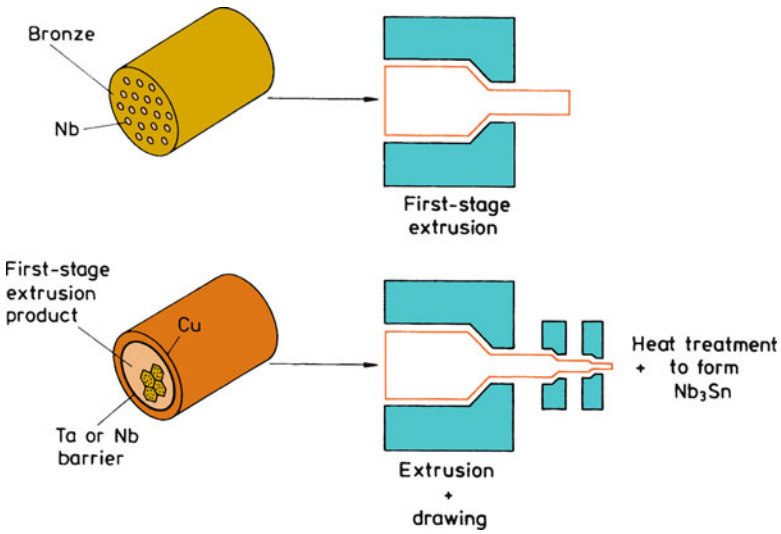

Fig. 9.8 Schematic of the bronze method of fabricating Nb_3Sn/Cu superconductor

long diffusion times. An example of an Nb_3Sn monolithic superconductor used in high-field magnets is shown in Fig. 9.9. Each little dot in this photograph (Fig. 9.9a) is a 4-μm Nb_3Sn filament. Wide strips in the hexagonal form are niobium; they serve as barriers to tin diffusion from the bronze into the copper. Tantalum is also used as a diffusion barrier. Figure 9.9b shows a scanning electron micrograph of a niobium/bronze composite before heat treatment to form Nb_3Sn. The good flux pinning and the consequent high critical currents in these superconductors are due to the grain boundaries (Scanlan et al. 1975; Nembach and Tachikawa 1979). At a heat treatment temperature of about 650–700 °C, the Nb_3Sn forms and consists of very fine grains, less than 80 nm (0.08 μm) in diameter. The critical current density for Nb_3Sn under these conditions is more than 2×10^5 A/cm^2 at 10 T and 4.2 K.

The problem of thermal mismatch, i.e., the differential expansion or contraction between the components of a composite (Chawla 1973a, b), something very much inherent to composites, also exists in superconductors. In the case of A15-type composite superconductors, their brittle nature makes this thermal mismatch problem of great importance. It turns out that in this case, when cooled from the reaction temperature (~1,000 K) to 4.2 K, the different coefficients of thermal expansion of copper and Nb_3Sn lead to rather large compressive strains in the brittle Nb_3Sn filament. Luhman and Suenaga (1976) showed that the T_c of Nb_3Sn varied with the strain applied to the Nb_3Sn filament by the copper matrix. Later, measurements of critical currents as a function of applied strain confirmed these results, and one could explain the strain-critical current behavior in terms of the effects of strain on T_c and H_{c2}. This understanding of strain-critical current behavior is used to good effect in the design of Nb_3Sn superconducting magnets. As pointed out, Nb_3Sn filaments fail at a tensile strain of about 0.2 %. Thus, if the superconductor is designed so that the Nb_3Sn filaments in the bronze matrix experience compression between 0.4 and 0.6 %, then one can expect these composites to withstand applied strains of between 0.6 and 0.8 % before fracture ensues in the Nb_3Sn filaments.

Although the bronze route of manufacturing the superconductor is a commercial process now, there are some disadvantages involved. One must have frequent interruptions for annealing the work-hardened bronze matrix. To shorten this process of fabrication, a number of in situ and powder metallurgy techniques have been tried (Roberge and Foner 1980). These in situ techniques involve melting of copper-rich Cu–Nb mixtures (~1,800–1,850 °C), homogenization, and casting. Niobium is practically insoluble in copper at ambient temperature. Thus, the casting has a microstructure consisting of niobium precipitates in a copper matrix. When this is cold drawn into wire, niobium is converted into fine filaments in the copper matrix. Tin is then plated onto the wire and diffused to form Nb_3Sn. The different melting and cooling techniques used include chill casting, continuous casting, levitation melting, and consumable electrode arc melting. The powder metallurgy techniques involve mixing of copper and niobium powder, pressing, hot or cold extrusion, and drawing to a fine wire that is coated or reacted with tin. The contamination of niobium with oxygen causes embrittlement and prevents its

conversion into fine filaments. This has led to the addition of a third element (Al, Zr, Mg, or Ca) to the Cu–Nb mixture. This third element preferentially binds oxygen and leaves the niobium ductile.

A summary of characteristics of Nb/Ti and Nb_3Sn multifilamentary composites is provided in Table 9.1.

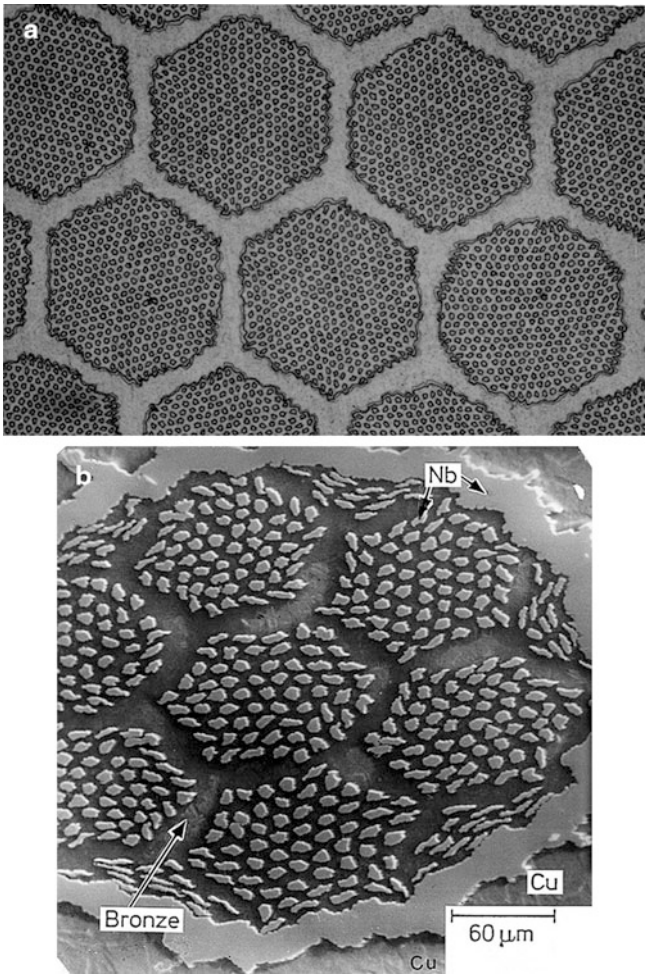

Fig. 9.9 (**a**) An Nb_3Sn/Cu composite superconductor used in high-field magnets. Each little dot in this picture is a 4-μm diameter Nb_3Sn filament. Hexagonal strips are niobium diffusion barriers for tin (courtesy of Hitachi Cable Co.). (**b**) Scanning electron micrograph of a niobium/bronze composite before the heat treatment to form Nb_3Sn

Table 9.1 A summary of characteristics of Nb–Ti and Nb_3Sn-type multifilamentary composites (after Hillmann 1981)

Characteristic	Nb–Ti	Nb_3Sn
T_c	≈9 K	18.1 K
B_{c2}	≈14.5 K	24.5 K
Stabilization	Simple, coextrusion with high-purity Cu matrix	Complex, coprocessing with bronze matrix, followed by heat treatment to obtain Nb_3Sn in a Cu matrix
Insulation	Conventional; varnish, cotton, and polymeric tape can be used	Complex, in prereaction insulated conductors, high thermal stability of insulation is needed; in post-reaction insulated conductors, careful mechanical handling is required
Advantages	Fabrication process is cheap; insensitive to mechanical handing, simple magnet technology	Applications to high magnetic fields and high temperatures
Disadvantages	Applications limited to 8 T at 4.2 K	Brittleness of the Nb_3Sn, restricted mechanical handling, large number of very fine filaments (diameter ≤5 μm) is required, complicated magnet winding

9.3.3 Ceramic Superconductors

The ceramic oxide superconductors with a transition temperature higher than the conventional superconductors were discovered in late 1986 and early 1987. Since then many oxide superconductors have been discovered, and they have a range of critical transition temperatures. There are two classes of high temperature superconductors (HTS): First Generation (1G) and Second Generation (2G). Also there is a rather complex notation that is commonly used in the ceramic oxide superconductor literature. For example, the oxides used in 1G HTS are bismuth-based, the one-layer compound $Bi_2Sr_2Cu_1O_y$ is denoted by (2210), the two-layer compound $Bi_2Sr_2Ca_1Cu_2O_y$ is designated by (BSCCO) or (2212), and the three-layer compound $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ is denoted by (Pb) (2223). 2G HTS are yttrium based, specifically YBa_2Cu_3O (referred to as YBCO). In fact, YBCO was one of the earlier oxide superconductors; interest in it waned when it was discovered that bismuth-based superconductors could carry more current in the presence of low magnetic fields. Oxide superconductors with a transition temperature around 90 K are available. The reader will recall that such high transition temperatures enable the use of liquid nitrogen (boiling point 77 K), a cheap and easily available coolant. With conventional superconductors, one must use liquid helium as a coolant. There are still many problems with these high-T_c superconductors; one of the major ones is that they carry very low current densities, especially in the presence of magnetic fields. The electrical resistance goes to zero at a T_c of 90 K,

but the supercurrents have difficulty going from one grain to another. Various explanations, such as impurities and misaligned grains, have been put forth to explain this behavior. The performance of these new superconductors deteriorates with increasing magnetic field. At a magnetic field of 1 T, the critical current density, J_c, is between 1 and 10 A/cm^2. The conventional superconductors, on the other hand, can carry as much as 10^5 A/cm^2.

Understandably, a large amount of research and development effort has been focused on wire and system development. HTS wire must be flexible and strong and capable of carrying large currents in the presence of a magnetic field. The key parameters in making a HTS wire system commercially successful are critical current density, operating temperature (related to but less than the critical temperature), magnetic field, and last but not least, cost. Critical current is the amount of current a given wire can carry without losing superconductivity. It would be desirable to have a J_c value between 10^3 and 10^5 A/cm^2. HTS wires must be able to carry current at relatively high temperatures to decrease the difficulties associated with cooling. The anticipated range for HTS operating temperature (depending on the application) is 4.2–77 K. Superconducting devices also require tolerance to surrounding magnetic fields and should be able to operate in the presence of magnetic fields. The goal for a cost-effective HTS wire is \$0.01/Am.

We alluded earlier to the extreme brittleness of the ceramic superconductors. Very powerful tensile and shear forces develop in dipole magnets due to the phenomenon of Lorentz force, enough to literally explode the ceramic oxides. This also means that processing of such superconductors into long lengths is much more difficult than is the case with a ductile Nb–Ti system. Since the discovery of HTS, many techniques have been tried to make HTS in the form of flexible, long conductor wires. One method called the *oxide-powder-in-tube* (OPIT) method (Sandhage et al. 1991) involved the use of oxide powder of appropriate composition (stoichiometry, phase content, purity, etc.) packed in silver tube (4–7 mm inside diameter and 6–11 mm outside diameter). The silver tube is sealed after packing and degassed. The deformation processing techniques commonly used are swaging and drawing for wires and rolling is used for tapes. Heat treatments, intermediate and/or subsequent to deformation, are given to form the correct phase, to promote grain interconnectivity and crystallographic alignment of the oxide, and to obtain proper oxygenation (Sandhage et al. 1991). Figure 9.10 shows a schematic of this process. What we need is a high degree of crystallographic alignment of the superconducting oxide grains. It is known that the critical current density in HTS is increased with the alignment of oxide grains (Osamura et al. 1990; Uno et al. 1991). A major obstacle in the manufacture of long lengths of YBCO wire is the existence of weak links, such as a grain boundary. Also, the use of silver as the matrix makes it very expensive.

In a manner similar to the so-called bronze route of making conventional superconductors, where the superconductor is a very brittle intermetallic, Nb_3Sn, one must avoid the synthesis of the brittle ceramic until the very end. The sintering step should be carried after the formation of the desired shape. This technique,

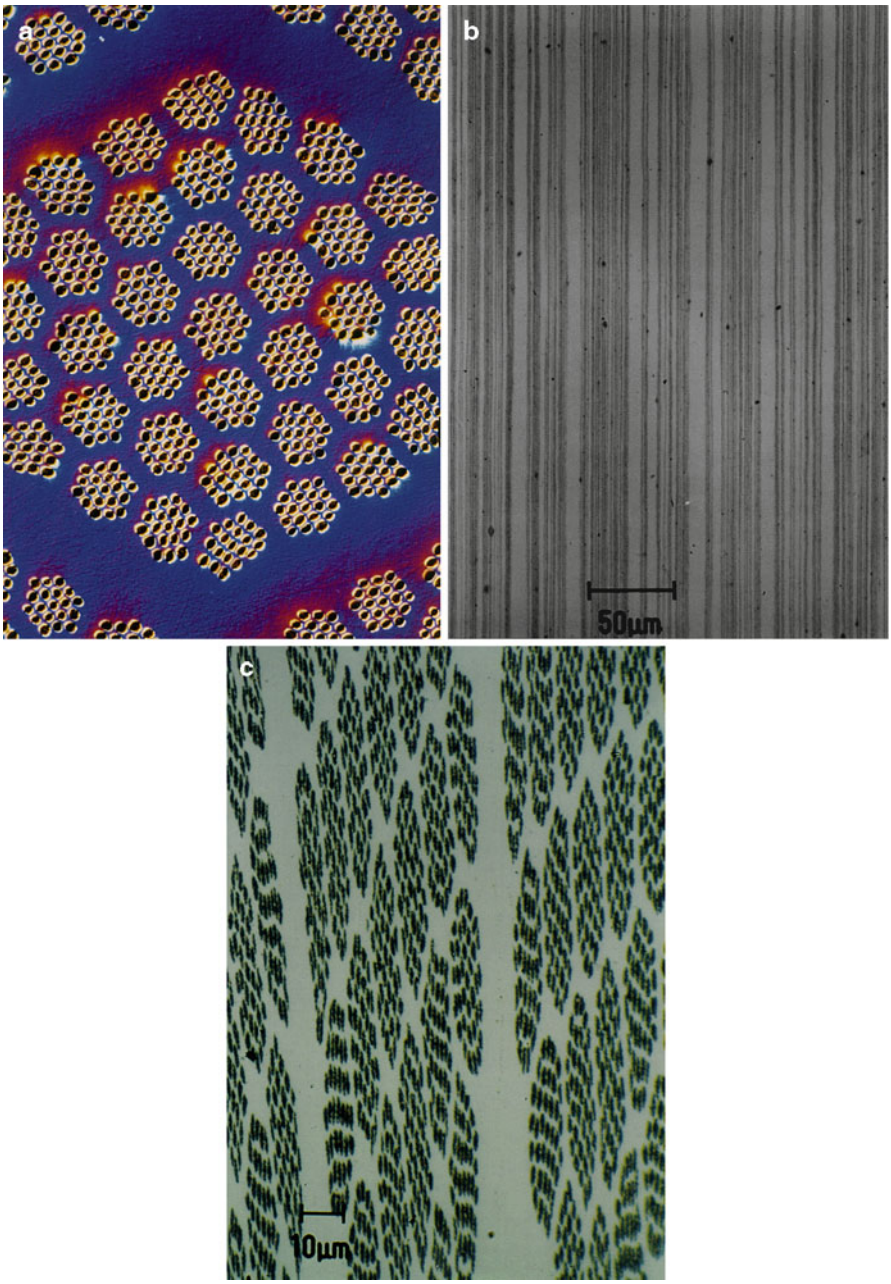

Fig. 9.10 (**a**) Low-magnification cross-sectional picture of a cable made by the MP process. (**b**) Longitudinal section and (**c**) transverse section. The superconductor is $Y_{0.9}$ $Ca_{0.1}$ Ba_2 Cu_4 $Ag_{0.65}$ metallic precursor/silver composite containing 962,407 filaments (courtesy of American Superconductor Co.)

called the *metallic precursor* (MP) method, involves melting the metallic elements (e.g., Y, Ca, Ba, Cu, and Ag), melt spinning, i.e., rapidly solidifying, the molten alloy into a ribbon form, and then pulverizing it to obtain homogeneous alloy powder. This precursor alloy powder is then packed into a silver can, sealed, and extruded into a hexagonal rod. Pieces of the extruded rod are packed into another bundle and further extruded. The final step in this process involves a very large reduction, up to 300:1, and results in round wire or tape (Masur et al. 1994). Figure 9.11a shows a low-magnification cross-sectional picture of a cable made by the MP process. Higher magnification views of the longitudinal section and transverse cross section of Y-124 (or more precisely, $Y_{0.9}$ $Ca_{0.1}$ Ba_2 Cu_4 $Ag_{0.65}$) metallic precursor/silver composite containing 962,407 filaments are shown in Fig. 9.11b. The uniformity of deformation is excellent. The extruded composites are then internally oxidized to form oxides: Y_2O_3, BaO, CuO, and Ba_2Cu_3O. These are then reacted to give the Y-124 phase. The precursor oxides are approximately 50% converted to Y-124 after 100 min at 700 °C and 80% converted after 300 min at 750°C (Masur et al. 1994). The tapes, after the oxidation treatment, are subjected to a thermomechanical treatment (TMT) to obtain suitable textures. The TMT involves multiple heat treatments in the 600–825 °C range, uniaxial pressings at pressure of up to 2 GPa, and the final heat treatment at 750 °C for 100 h in one-atmosphere oxygen. Recall the similarity between this and the bronze process used for Nb_3Sn.

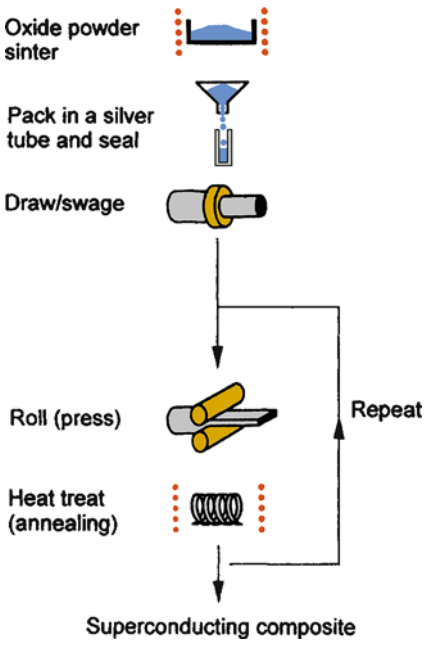

Fig. 9.11 Schematic of the oxide powder in the tube method of making high-temperature superconducting composite [after Sandhage et al. (1991)]

One of the key developments in regard to HTS was the demonstration that crystallographic texture could be introduced into metal by rolling and annealing the metal into a thin tape, and this texture could be transferred to a superconducting oxide coating through buffer layers deposited on the metallic template. The buffer layers also serve to prevent any unwanted coating-substrate chemical reactions. The result was a superconducting oxide, such as yttrium–barium–copper oxide (YBCO), with oriented crystals. Such a tape can conduct large electrical currents without resistance at liquid nitrogen temperature (77 K). Although American Superconductor's first-generation, or 1G, HTS wires are in commercial use, second-generation (2G) wires are expected to be a formed-fit replacement for 1G wire. Eliminating silver in the manufacturing process will make the 2G wire less expensive. Also, 2G wire will work better than 1G wire in the presence of a strong magnetic field in a motor, generator, or transformer.

We now briefly describe two important processes of obtaining aligned grains of oxide superconductors. The first one, called ion beam assisted deposition technique (IBAD), starts with a randomly oriented sheet of Hastelloy (a nickel alloy) on which a yttrium-stabilized zirconia (YSZ) layer is deposited as a buffer. The ion beam selectively removes the YSZ atoms that are not aligned at certain orientations biaxially. YBCO film is then deposited on this template. This process is based on some earlier Japanese work and the work done at the Los Alamos National Laboratory in the USA. The second process, developed at the Oak Ridge National Laboratory, is called "rolling assisted biaxially textured substrates," or RABiTS (Goyal et al. 1999; Bhattacharjee et al. 2007). This results in a biaxial texture in a range of metals. On this textured metallic substrate, oxide superconductors are deposited epitaxially. These textured substrates serve as structural templates for the final superconductor layer, which has substantially fewer weak links. In the RABiTS process, silver is replaced by nickel or nickel alloys, eliminating the expensive silver. The RABiTS process consists of the following steps:

1. Thermomechanical processing (rolling, heat treatments, and annealing) is used to obtain flexible, biaxially oriented Ni or Ni alloy substrates. The substrate serves as a structural template for the superconducting YBCO layer, which has substantially fewer weak links than the substrate. This is shown in Fig. 9.12. The circles show the pole figures showing the specific type of grain texture obtained.
2. Deposit a series of buffer layers on the substrate. YBCO superconductors are then deposited epitaxially on the buffer layer. The buffer layers transfer the texture of the metal substrate to the superconductor and prevent any reaction between the substrate and the superconductor. The final composite superconducting tape is shown schematically in Fig. 9.13.

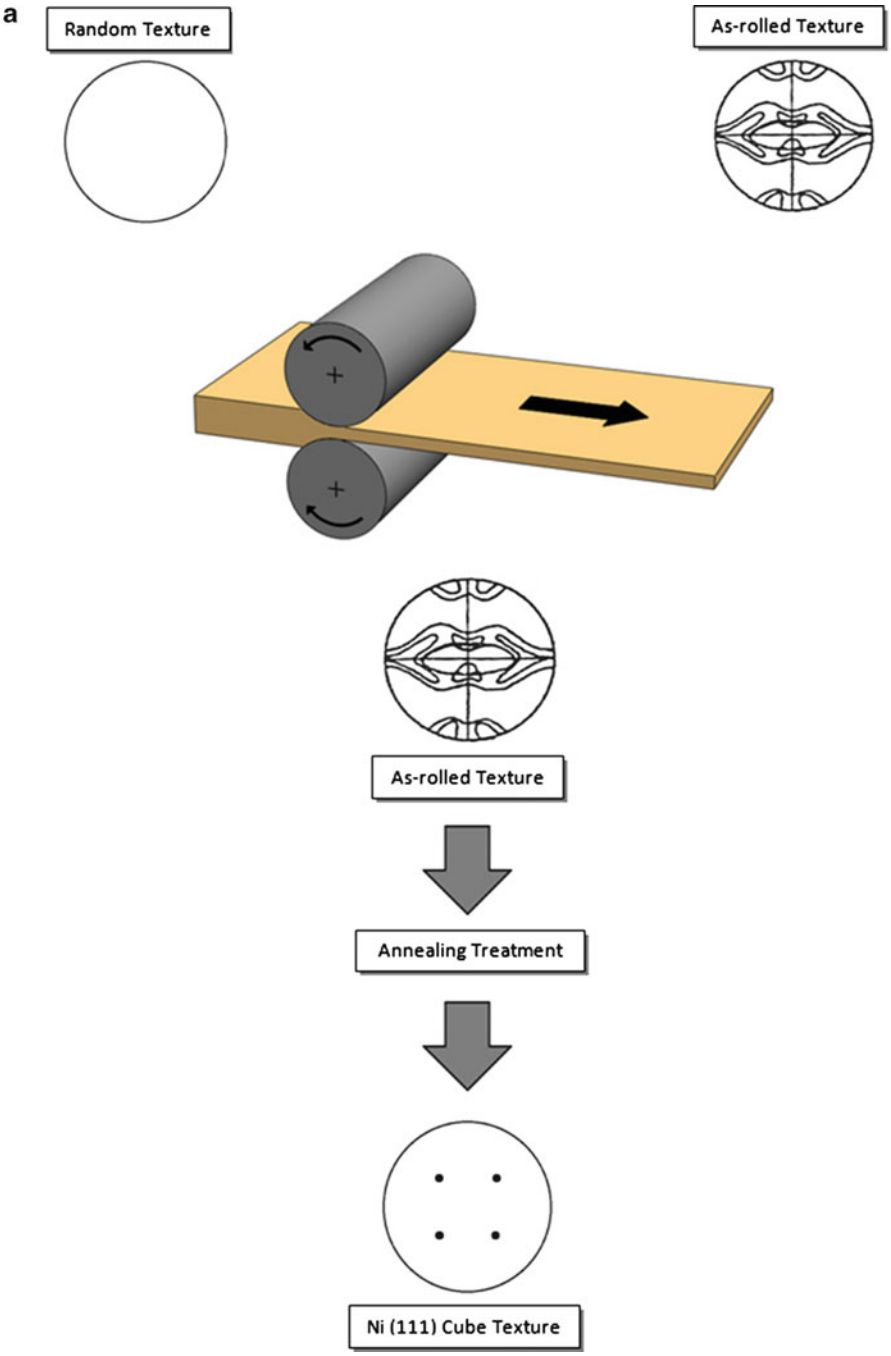

Fig. 9.12 The RABiTS process. A metallic substrate is prepared by rolling and heat treatments to serve as a structural template for the superconducting YBCO layer, which has substantially fewer weak links than the substrate. The *circles* show the pole figures showing the specific type of grain texture obtained. (**a**) Cube texture in Ni (**b**) Final superconducting tape on Ni

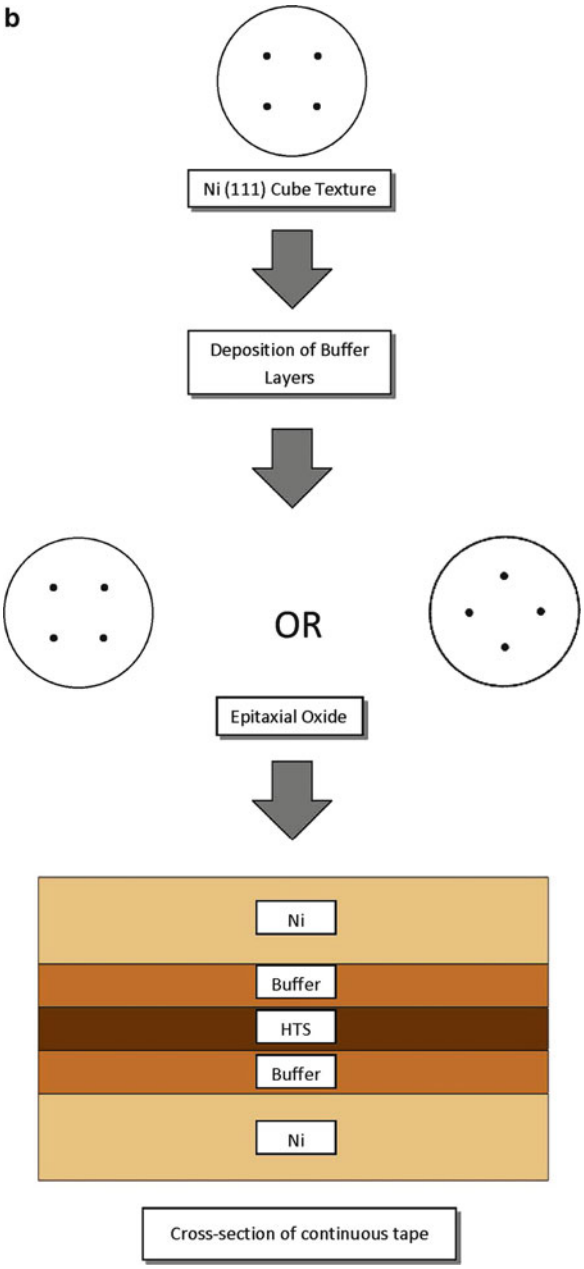

Fig. 9.12 (continued)

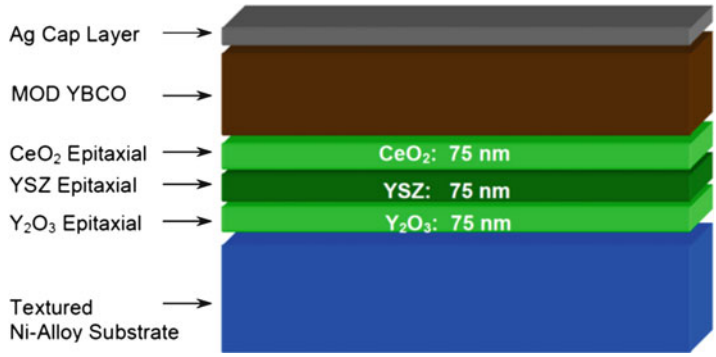

Fig. 9.13 A schematic of final composite superconducting tape obtained by the RABiTS process. The series of buffer layers and the YBCO superconductor are deposited epitaxially on the substrate. The buffer layers transfer the texture of the metal substrate to the superconductor and prevent any reaction between the substrate and the superconductor

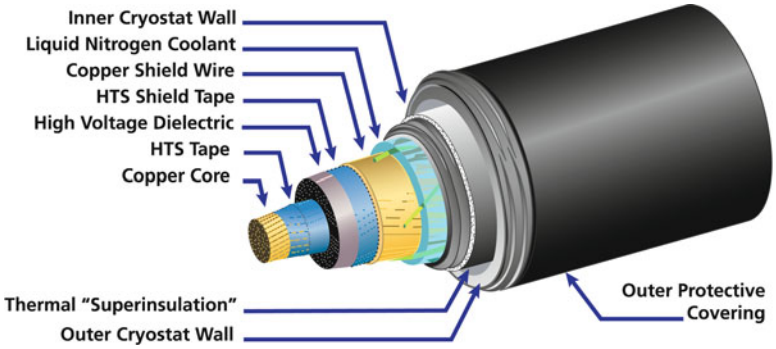

Fig. 9.14 A schematic of a 2G superconducting cable, trade name Amperium. Note the number of different materials used (courtesy of American Superconductor Co.)

American Superconductor Co. makes HTS wires that are high-performance, long-length, RABiTS-based, nickel–tungsten substrate coated with very thin buffer layers. The company produces wide ribbons of material that are slit into 100-m-long, 4-mm-wide wires. Figure 9.14 shows such a superconducting cable, trade name Amperium. An impressive array of different materials is used to make the superconducting cable.

9.4 Applications

Filamentary superconducting composites have some very important applications. Examples of applications of metal matrix composite superconducting coils include (Cyrot and Pavuna 1992):

- High-field magnets for research in high energy and in condensed matter physics.
- Magnetic resonance imaging (MRI), which requires extremely uniform magnetic fields of ~1–2 T.
- Coils for windings in motors and generators.
- Magnetic levitating (MAGLEV) coils for high-speed trains.
- Magnetohydrodynamic and electromagnetic thrust systems for propulsion in ships and submarines.

Since the discovery of HTS, much emphasis has been placed on the high T_c of these superconductors. It is good to remember a rule-of-thumb for most superconductor applications, which says that critical temperature T_c of a technological superconductor should be about twice the use temperature (Cyrot and Pavuna 1992), i.e.,

$$T_{use} \sim T_c/2.$$

This implies that superconductors that are used with liquid helium (4.2 K) as a coolant should have a $T_c > 8$ K. In fact, due to the heating of the magnet, the actual operational temperature is closer to ~7 K, so one needs a $T_c \sim 15$ K. Thus, to use the oxide high-temperature superconductors (HTS) in applications at 77 K one needs a superconductor with a $T_c \sim 150$ K. Such a material has not yet been synthesized; the thallium-compound with $T_c \sim 125$ K would appear to be the best candidate for the "true" technological material at liquid nitrogen temperature. For most electronic-type applications, the rule of thumb is less stringent, and we can write:

$$T_{use} \sim 2/3\, T_c.$$

Nb_3Sn/Cu superconducting composites are used for magnetic fields greater than 12 *T*. Such high fields are encountered in thermonuclear fusion reactors, and superconducting composite magnets would represent a sizable fraction of the capital cost of such a fusion power plant. Table 9.2 shows the requirements for critical current density in a given magnetic field for several applications of superconductors. The performance of superconducting magnets will affect the plasma as well as the plasma density—and hence the importance of materials research aimed at improving the performance limits of these superconducting magnets. The main difference between the magnets used in a fusion reactor and in power transmission is that the former use superconductors at very high magnetic fields while the latter use them at low fields.

Table 9.2 Critical current density in a given magnetic field for several applications of superconductors (after Cyrot and Pavuna 1992)

Application	B (T)	J_c (A/cm^2)
Interconnects	0.1	5×10^6
AC transmission lines	0.2	10^5
DC transmission lines	0.2	2×10^4
SQUIDs	0.1	2×10^2
Motors and generators	~4	~10^4
Fault current limiters	>5	>10^5

A large scale potential application of Nb–Ti/Cu superconducting magnets is in magnetically levitated trains. Japan National Railways has tested such trains over a small stretch at speeds over 500 km/h. Nb–Ti/Cu superconductor composites are also employed in pulsed magnets for particle accelerators in high-energy physics. Other applications of these superconductors include the fields of magnetohydrodynamics and power. Superconducting electric generators for utility applications allow two times or more kilovoltamperes of electricity to be produced than by a conventional generator of a comparable size. The field windings can be made from a Nb–Ti/Cu composite or HTS composites. By using superconducting materials, the designers could make a generator that developed a much stronger magnetic field than a conventional generator, permitting a significant reduction in the size of the generator for the same power output. Superconducting magnets do require cryogenic temperatures to operate, but the cost of this refrigeration is more than compensated by the energy savings. One has only to remember that, in a superconducting machine working with almost zero resistance, the normal losses associated with the flow of electricity in rotor windings of a conventional machine are absent, resulting in a higher efficiency and reduced operating costs. A major problem in this development of superconducting generators is to prevent the movement of rotor windings under the intense centrifugal and magnetic forces exerted on them. The rotor spins at a speed of 360 rpm. Thus, even an infinitesimally small movement of these components would generate enough heat by friction to quench the superconductors. One solution used by the GE researchers involved a special vacuum epoxy-impregnation process to bond the Nb–Ti superconductors into rock solid modules and strong aluminum supports to hold the windings rigidly.

An electrical transformer, built by ABB, using 1G HTS wires has been in use in Geneva, Switzerland since 1997. This transformer used the flexible HTS wires made by American Superconductor. The process involves packing of the raw material into hollow silver tubes, drawing into fine filaments, grouping the multifilaments in another metal jacket, further drawing and heat treating to convert the raw material into the oxide superconductor (see Sect. 9.3.3). The wire is then flattened into a ribbon (2.5 $\times$ 0.25 mm) that is used to make the transformer coils. The transformer contains 6 km of HTS wires wound into coils, immersed in liquid nitrogen. According to ABB this transformer loses only about one fifth of the ac power losses of the conventional ones. Because HTS wires can carry a higher current density, this new transformer is more compact and lighter than a

conventional transformer. It should also be mentioned that liquid nitrogen used as a coolant in the HTS transformer is safer than oils used as insulators in conventional transformers.

Finally, we describe a very important application of Nb-based superconducting composites.

9.4.1 Magnetic Resonance Imaging

The phenomenon of nuclear magnetic resonance (NMR) is exploited in the technique of magnetic resonance imaging (MRI). This technique has a major advantage over X-ray radiography in that it is a noninvasive diagnostic technique, and thus the human body is not exposed to an ionizing radiation. It would be useful to briefly explain the principle behind this important technique. Use is made of the electromagnetic characteristics of the nuclei of elements such as hydrogen, carbon, and phosphorus that are present in the human body. The nuclei of these elements act as bar magnets when placed in a strong magnetic field. The patient is placed in the center of a very powerful magnet. When the magnetic field is turned on, the nuclei of the elements in the patient's body part under examination realign along the magnetic field direction. If we apply a radiofrequency field, the nuclei will reorient. And if we repeat this process over and over again, the nuclei will resonate. The resonance frequency is picked up by a sensitive antenna, amplified, and processed by a computer into an image. The MRI images, obtained from the resonance patterns are more detailed and have a higher resolution than traditional techniques of visualization of soft tissues. And best of all, these images are obtained without exposing the patient to a radiation or performing biopsy.

MRI became a major diagnostic tool after solenoids made of metal matrix composites consisting of continuous fiber (Nb–Ti) in copper matrix became commercially available. Of course, MRI techniques do not have to use superconducting magnets, i.e., other magnets can be used. There are, however, certain advantages with superconductors: better homogeneity and resolution of magnetic fields and higher field strengths than are available with conventional magnets. The disadvantage is that higher fields with superconductors lead to greater shielding problems. The superconducting solenoid, made from Nb–Ti/Cu composite wire, is immersed in a liquid helium cryogenic dewar. The liquid helium is consumed at about 4 ml/h, and each refill of the dewar lasts about 3 months. Commercially manufactured NMR (nuclear magnetic resonance) spectrometer systems, also called magnetic resonance imaging systems, for medical diagnostics became available in the 1980s; Fig. 9.15 shows one such system. It should be pointed out no ferromagnetic articles should be brought in the vicinity of an MRI superconductor.

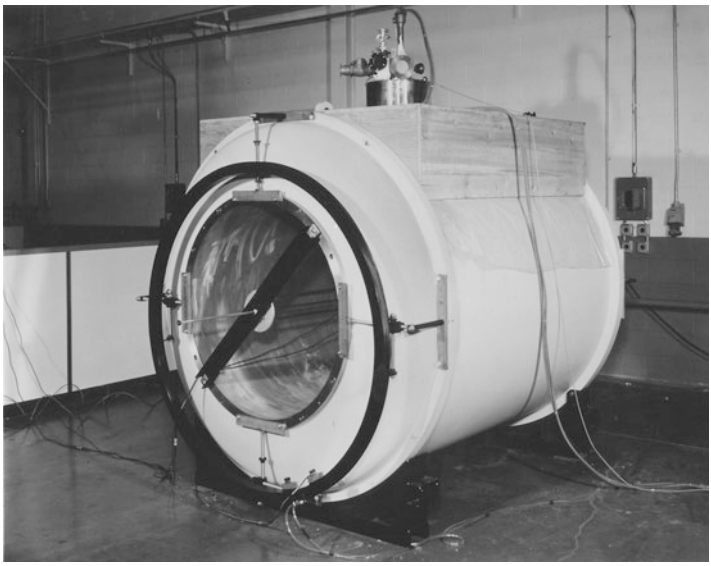

Fig. 9.15 A magnetic resonance imaging system for clinical diagnostics, under preparation (courtesy of Oxford-Airco)

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Further Reading

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Problems

9.1. There are many known superconducting A15 compounds. Of these Nb_3Al, Nb_3Ga, and Nb_3Ge have higher values of T_c and H_{c2} than do Nb_3Sn and V_3Ga. How then does one explain the fact that only Nb_3Sn and to a lesser extent V_3Ga are available commercially?

9.2. It is believed that grain boundaries are the imperfections responsible for the flux-pinning in high-J_c materials like Nb_3Sn and V_3Ga. How does J_c vary with grain size?

9.3. What is the effect of any excess unreacted bronze leftover in the manufacture of Nb_3Sn superconductor composite via the bronze route?

9.4. Examine the Nb–Sn phase diagram. At what temperature does the A15 compound (Nb_3Sn) become unstable? Nb_3Sn is formed by solid state diffusion in Nb/Cu–Sn composites at 700 °C or below. Is this in accord with information from the phase diagram? Explain.

9.5. Do you think it is important to study the effect of irradiation on superconducting materials? Why?

9.6. In the high magnetic field coils of large dimensions, rather large tensile and compressive loads can be encountered during energizing and deenergizing. Discuss the effects of cyclic stress on the superconducting coil materials.

9.7. Superconducting composites in large magnets can be subjected to high mechanical loads. Describe the sources of such loadings.