Chapter 3 MATRIX MATERIALS

A wide range of metals and their alloys may be used as matrix materials. In this chapter, we review some of the basic concepts and fundamentals of bonding and structure of common metals. Following this, we provide a summary of the characteristics of some of the most common metals that are used as matrix materials in metal matrix composites.

3.1 BONDING AND CRYSTALLINE STRUCTURE IN METALS

Metals are characterized by metallic bonding, i.e., valence electrons are not bound to a particular ion in the solid. A "sea of electrons" surrounds positively charged atomic nuclei. A major result of this electron cloud surrounding the atomic nuclei is that the electronic bonding in metals is nondirectional. This non-directionally of bonding is very important since it contributes to isotropy in many properties.

When cooled down from their molten state, most metals assume a crystalline structure below their melting point. Some metals and alloys do not undergo crystallization and assume an amorphous structure, but only at very high cooling rates (> 10^6 Ks^{-1}). The basic difference between a crystalline and non-crystalline structure is the degree of ordering. A fully crystalline state has a high degree of order. Metal ions are quite small (diameter ~ 0.25 nm), so in a crystalline structure these ions are packed in a very regular and close-packed manner. Because of non-directional bonding, we can model the arrangement of atoms in the form of hard spheres.

There are two arrangements of packing of hard, identical spheres that result in close packed structures: Face centered cubic (FCC) and hexagonal close packed (HCP). There is a third arrangement that is observed in a number of metals, namely, body centered cubic (BCC). The BCC structure is more open than the FCC or HCP structure. Figure 3.1 shows the atomic arrangement in these three cases. Both HCP and FCC structures result in close-packed structures. The difference between the two results from the way the close packed planes are stacked. Figure 3.2(a) shows the stacking arrangement of the first layer (layer A) in a close packed structure. For the second layer of close packed atoms, one has the choice of putting the atoms at sites B or C, which are equivalent sites. The difference between FCC and HCP structures comes in the placement of the third layer of atoms. Assuming the B configuration for the second layer of atoms, one can have the third layer in A or C configuration. It turns out that the ABABAB... (or ACACAC...) results in HCP while the ABCABCABC... stacking sequence results in the FCC structure. Stacking faults or planar defects may be formed, where there is an interruption of ABCABCABC stacking (FCC) sequence such that we have an HCP region in an FCC structure.

3.2 CRYSTALLINE DEFECTS IN METALS

Most metals are crystalline in their solid state. Ideally, a metal crystal has



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Fig. 3.1 Three common crystal structures in metals, face centered cubic (FCC), body centered cubic (BCC), and hexagonal close packed (HCP).



Fig. 3.2 (a) A layer of close packed atoms (b) Positions of layers B and C on top of layer A. Close packed layers in FCC has ABCABC stacking, while HCP has ABAB... stacking sequence.

atoms arranged in a very orderly fashion in a three dimensional lattice. Such perfect crystals are rarely seen in practice. Generally, various kinds of imperfections are present. It turns out that many of the important and interesting properties of crystalline materials are due to the presence of these imperfections or defects in the crystalline lattice. These defects, called lattice defects, can be zero-, uni-, bi-, or tri-dimensional. The zero-dimensional defects are an extension of the order of the lattice constant (0.2–0.4 nm) in all three spatial directions. Common examples are vacancies and interstitial atoms, etc. Unidimensional or linear imperfections have atomic extensions in one spatial direction only. The most important example of a linear defect is a dislocation. Bi-dimensional defects have atomic extension in two spatial directions, for example, grain boundaries, twin boundaries, interfaces between phases, etc. Three-dimensional defects extend into three spatial directions, for example, second phase particles, pores, etc. These defects may result under less than ideal processing conditions.

Besides geometric differences, there is a very important physical difference between zero-dimensional defects and other higher-dimensional defects in crystals. Considering the free energy involved, only point defects (i.e., zero-dimensional) can be present in a state of thermal equilibrium in a crystal, while dislocations, grain boundaries, etc., represent energy much higher than energy represented by thermal fluctuation.

A dislocation can be described in terms of two vectors:

- (i) Dislocation line vector, t, which gives the direction of the dislocation line at any point. The vector t is parallel to the dislocation. In the case of a dislocation loop, the vector t runs along the loop length and will have opposite senses along the two opposite sides of the loop.
- (ii) Burgers vector, **b**. This indicates the magnitude and direction of the displacement of the part above the slip plane of a crystal with respect to the part below the slip plane. The Burgers vector **b** of a dislocation loop is constant, while the dislocation line vector **t** can change direction continuously. The Burgers vector is always an integral atomic spacing because the lattice must maintain atomic registry through the slipped and unslipped regions.

There are two special types of dislocations:

(a) Edge dislocation: the dislocation line vector and the Burgers vector are orthogonal, i.e., at ninety degrees.

(b) Screw dislocation: the dislocation line vector and the Burgers vector are parallel.

Dislocations control many important characteristics of materials. In particular, dislocations occupy a position of fundamental importance in the mechanical behavior of crystalline materials. Their presence reduces the force necessary to cause displacement of atoms. In this sense, dislocations act like a lever. They allow a given quantity of work to be done by a small force moving through a large distance rather than a large force moving through a small distance. Thus, plastic flow or plastic deformation in crystalline solids is accomplished by means of movement of dislocations. The plastic strain depends on the displacement caused by each dislocation, the density of *mobile* dislocations, and the average distance moved by a dislocation. When these linear defects move under the action of a shear stress, they result in slip or glide between crystal planes, which in turn results in permanent (plastic) deformation.

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Besides plastic deformation, there are many other physical and chemical properties that are affected by the presence of dislocations. For example, dislocations can serve as easy paths for atomic diffusion (which can affect creep behavior), precipitation reactions, and order processes. They can also be very efficient sites for nucleation of solid-state phase transformations, affect thermal and electrical conductivity, especially at very low temperatures, and affect the current carrying capacity in superconductors.

Planar or two-dimensional defects include external surfaces, grain boundaries, stacking faults, etc. The surface is treated as a planar imperfection because the surface atoms are not bonded to the maximum number of neighbors. Thus, the surface atoms are in a higher energy state than the atoms in the interior. Small angle grain boundaries consist of slight orientation mismatch (few degrees). Simple dislocation arrays form such boundaries: a wall of aligned edge dislocations forms a tilt boundary while screw dislocations form twist boundaries. When the degree of misorientation between grains is too large to be accommodated by dislocations, high angle grain boundaries are formed. These high angle grain boundaries have a higher energy at the grain boundaries than small angle grain boundaries. A twin boundary is a special type of grain boundary across which there is mirror symmetry of the lattice. The region of material between these boundaries is termed a twin. Twin boundaries can result from mechanical shear (mechanical twins) or annealing following deformation (annealing twins). Annealing twins are commonly observed in FCC crystals while mechanical twins are seen in BCC and HCP metals.

3.3 STRENGTHENING MECHANISMS IN METALS

Metals can be strengthened in a number of ways. We provide a summary of these inasmuch as many of these mechanisms influence the behavior of the metal matrix, and thus, of the composite. For a more thorough treatment of strengthening mechanisms, the reader is referred to Meyers and Chawla (2005).

3.3.1 Dislocation Strengthening

The presence of dislocations generates internal stress fields. Extra work needs to be done to move a dislocation through such internal stress fields of other dislocations. Various theories have been proposed to explain the strengthening due to increased dislocation density that results, for example, from subjecting a metal to cold working. Although the dislocation structure of a deformed metal, polycrystalline or single crystal, is inhomogeneous, the strengthening due to dislocation density results in the flow stress being proportional to the square root of the dislocation density, ρ :

$$\tau = \tau_0 + \alpha Gb \sqrt{\rho}$$

where τ is the shear flow stress, τ_0 is a friction stress, G is the shear modulus, b is the Burgers vector, ρ is the dislocation density, and α is a constant on the order of 0.5. As an example, copper, in an annealed condition, has a dislocation density, $\rho = 10^7$ cm⁻² while after some cold working, its dislocation density, ρ increases to 10^{12} cm⁻².

Plastic deformation in metals commonly occurs by the movement of dislocations. In HCP metals, plastic deformation can also occur by twinning. The presence of dislocations results in what is called strain hardening or work hardening in metals. Sometimes we also refer to this as dislocation strengthening. Obstacles to dislocation motion (other dislocations, solute atoms, precipitates, grain boundaries, etc.) produce strengthening at room temperature and intermediate temperatures. At high temperatures, thermal energy can help overcome these obstacles (i.e., dislocation climb).

3.3.2 Grain Boundary Strengthening

Grain boundaries can be a very effective source of strengthening at moderate temperatures. Commonly, this is referred to as the Hall-Petch equation and is written as:

$$\sigma_v = \sigma_o + kd^{-1/2}$$

where σ_y is the yield strength, σ_o is the friction stress, k is the Hall-Petch coefficient, and d is the average grain size. The dependence of strength on inverse square root of the grain size is strictly true only over a certain range of grain sizes. At very small grain size, especially in the nanometer grain scale, this equation does not hold. The exponent of d may also change with the grain size.

3.3.3 Solute and Precipitation Strengthening

Solute atoms (solid solution strengthening), precipitates (precipitation hardening) and dispersoids (dispersion strengthening) can also impede dislocation motion and strengthen the metal.

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Precipitation hardening is a versatile strengthening technique for some metallic alloys, especially aluminum, steels, and nickel-based alloys. Precipitation hardening comes about an aging treatment, which involves precipitating, out of a homogeneous supersaturated solid solution, a series of metastable and stable precipitates. Various structures offer different levels of resistance to dislocation motion. An example of precipitates formed in an aluminum alloy, 2080 alloy matrix in a composite after T6 heat treatment, is shown in the transmission electron micrograph in Fig. 3.3. This material was also subjected to cyclic fatigue, and dislocations, constrained by the particles, are also shown. Figure 3.4 shows, schematically, the variation of hardness with aging time for 2080 aluminum alloy for three different temperatures. Also shown are the different precipitate types that occur during the aging treatment. Peak hardness or strength corresponds to a critical dispersion of semi-coherent precipitates.

The shape of the aging curve can be explained as follows. Immediately after quenching, only solid solution hardening is predominant. At the onset of aging, coherent zones appear in the initial stages of aging, that are nothing but clusters of solute atoms on certain crystallographic plains of the matrix



Fig. 3.3 Precipitates (S') and dispersoids (Al₃Zr) formed in aluminum alloy 2080 (Ganesh and Chawla, 2004). The transmission electron micrograph shows the precipitate structure in the matrix of a fatigued $2080/\text{SiC}/10_p$ composite (<220> zone axis). Dislocation motion is constrained by the precipitates and dispersoid particles.



Fig. 3.4 Schematic of the variation of hardness with aging time in a 2080 (Al-Cu-Mg) aluminum alloy. Peak hardness or strength corresponds to a critical dispersion of coherent or semi-coherent precipitates. With increasing temperature, the time to peak aging decreases, because of the acceleration in aging.

(e.g., clustering of copper atoms on {100} planes of aluminum). These zones are transition structures and are referred to as Guinier-Preston zones. We call them zones rather than precipitates in order to emphasize the fact that zones represent a small cluster of solute atoms which have not yet taken the form of precipitate particles. The very small GP zones are coherent with the matrix, i.e., the lattice planes cross the interface in a continuous manner and small elastic, coherency strains in the matrix are present. With increasing aging time, these zones grow or thicken by diffusion. As they grow, the misfit strains between the precipitate and matrix increase. Along some planes, coherency is lost, and dislocations form at the interface to take up the strain. Thus, the elastic energy associated with coherency strains along specific planes is reduced. The overall strain field around the particle, however, increases because of the newly-formed dislocations, as well as coherency strains on other planes. This increases the resistance to dislocation motion and increases the strength of the alloy. Further growth of these semi-coherent zones or precipitates results in a complete loss of coherency; an incoherent interface forms between the precipitate and the matrix.

The hardness increases as the GP zone size increases with time, making it more difficult for the dislocations to shear them. With a further increase in aging time, equilibrium precipitates with incoherent interface start appearing and the mechanism of dislocation bowing (called Orowan bowing) around the particles becomes operative. The peak hardness or strength is associated with a critical dispersion of coherent or semi-coherent precipitates. At this point, the contributions from shearing and by-pass of precipitates is equal. Further aging results in an increase of the interparticle distance and a lower strength results as dislocation bowing becomes easier.

Dislocations move on specific slip planes in a metal under the action of a shear stress. If the slip plane has obstacles penetrating it, e.g., precipitates or dispersoids, a dislocation moving on this slip plane must interact with these obstacles. The dislocation, under the action of an applied shear stress, τ , bows between the obstacles in the slip plane. If we ignore the changes in the orientation of the dislocation because of bowing, the shear stress required to bow the dislocation to a radius r is given by:

$$\tau = \frac{\mathrm{Gb}}{2\mathrm{r}}$$

where G is he shear modulus of the metal and b is its Burgers vector. This mechanism of dislocation bowing around particles is called Orowan bowing.

3.3.4 Fracture in Metals

Generally, metals are quite ductile and fracture by a process known as microvoid coalescence. In this process, also referred to as dimple facture, microvoids nucleate at precipitate particles, inclusions, etc. Under applied stress, these microvoids grow and coalesce leading to final fracture with characteristic dimples on the fracture surface. Figure 3.5(a) shows schematically the process while 3.5(b) shows an SEM micrograph of an actual fracture surface obtained after tensile testing in an aluminum alloy. Note the presence of precipitates, in the center of dimples, where microvoids nucleated.

3.4 COMMON MATRIX MATERIALS

3.4.1 Aluminum and Aluminum Alloys

Aluminum alloys, because of their low density and excellent strength, toughness, and corrosion resistance, have been used extensively in the automotive and aerospace fields. Of special mention are Al-Cu-Mg and Al-Zn-Mg-Cu alloys, which are very important precipitation hardenable alloys.



Fig. 3.5 (a) Schematic of nucleation, growth, and calescence of microvoids at precipitate particles in a ductile metallic alloy, (b) Characteristic dimples on the fracture surface in an aluminum alloy. Note the presence of precipitate particles that served as the nucleating sites for microvoids. (Chawla et al., 2002).

Aluminum alloys can be classified as cast, wrought, or age-hardenable alloys. Some of the common age-hardening or precipitation-hardenable treatments for Al alloys are the following:

- 1. T4: Solutionizing and quenching, followed by aging at room temperature, or "natural aging."
- 2. T6: Solutionizing and quenching, followed by aging at a temperature above room temperature (120-190°C), or "peakaging."
- 3. T7x: Solutionizing, quenching, and overaging.
- 4. T8xx: Solutionizing, quenching, cold working, and peak-aging.

The solutionizing temperature is typically between 440 and 540°C, while the quenching medium can be water or a synthetic quenchant.

Liquid aluminum, like most metals, has a very low viscosity, which makes for easy casting practice. The temperature dependence of viscosity of liquid aluminum is given by (Smithells, 1976):

$$\eta = 0.1492 \exp(1984.5/T)$$

where η is the viscosity in MPa.s, R is the gas constant (= 8.3144 J/K mol), and T is the temperature in Kelvin. At its melting point, pure aluminum has a viscosity of $\sim \eta = 12$ MPa.s. The addition of ceramic particles or inclusions raises the viscosity very quickly. This has important implications in the processing of particle reinforced metal matrix composites (see chapter 4).

3.4.2 Titanium Alloys

Titanium is one of the most important aerospace materials. Pure titanium has a density of 4.5 gcm⁻³ and a Young's modulus of 115 GPa. For titanium alloys, the density can vary between 4.3 and 5.1 gcm⁻³ while the Young's modulus can range between 80 and 130 GPa. Thus, titanium and its alloys have relatively high strength/weight and modulus/weight ratios. Titanium has a relatively high melting point (1672°C) and retains strength to high temperatures with good oxidation and corrosion resistance. All these factors make it an ideal material for aerospace applications. Titanium alloys are used in jet engine (turbine and compressor blades), fuselage parts, etc. It is, however, an expensive material.

At extremely high speeds, such as in a supersonic military aircraft, the skin of an airplane heats up so much that aluminum alloys are no longer an option. Titanium alloys must be used at such high temperatures. In a supersonic plane, flying at speeds over Mach 2, the temperatures will be even higher than what titanium alloys can withstand. Titanium aluminides are one of the candidate materials in this case.

Titanium has two polymorphs; alpha (α) titanium has an HCP structure and is stable below 885°C and beta (β) titanium which has a BCC structure and is stable above 885°C. Aluminum raises the $\alpha \rightarrow \beta$ transformation temperature, i.e., aluminum is an alpha stabilizer. Most other alloying elements (Fe, Mn, Cr, Mo, V, No, Ta) lower the $\alpha \rightarrow \beta$ transformation temperature, i.e., they stabilize the phase. Thus, three general alloy types can be produced, viz., α , $\alpha+\beta$, and β titanium alloys. The Ti-6%Al-4% V, called the *work horse* Ti alloy of the aerospace industry, belongs to the ($\alpha+\beta$) group. Most titanium alloys are used after hot working in the ($\alpha+\beta$) region, which breaks the structure and distributes the β phase in an extremely fine form.

Titanium has a great affinity for oxygen, nitrogen, and hydrogen. Parts per million of such interstitials in titanium can change mechanical properties drastically. In particular, these microstructural changes may result in severe embrittlement. This is why welding of titanium by any technique requires protection from the atmosphere. Electron beam techniques, in vacuum, are also frequently used.

3.4.3 Magnesium and its Alloys

Magnesium and its alloys form another group of light metals. Magnesium is one of the lightest metals, its density being 1.74 gcm⁻³. Magnesium alloys, especially castings, are used in automotive and aircraft gearbox housings, chain saw housing, laptop casings, electronic equipment, etc. Magnesium has a hexagonal close-packed structure, which gives it limited ability to deform plastically by slip at room temperature.

3.4.4 Cobalt

Cobalt is a very common metal matrix that is used in WC/Co composites, also known as cemented carbides, which are used as inserts for cutting tool and in oil drilling. During processing of cemented carbides, cobalt is used in a powder form. Cobalt powder can be produced chemically by hydrogen reduction or atomization of cobalt liquid. The chemistry and crystal structure of Co powder are different from that of Co matrix in a WC/Co composite. Milling and processing by liquid-phase sintering or high-temperature, high-pressure compaction can affect the chemistry of the finished Co matrix.

Pure Co is stable below 417°C in the HCP crystal structure. Above this temperature, the high-temperature face centered cubic (FCC) structure is stable. It turns out that the FCC cobalt becomes stable at room temperature because of dissolution of carbon from WC during processing of WC/Co composites. The FCC structure has more slip systems available, which results in higher ductility. In WC/Co composites, the small amount of Co matrix holds the WC particles in place and provides toughness, which stems from its ability to deform plastically.

3.4.5 Copper

Copper has a face centered cubic structure. Because of its high electrical conductivity (only silver and gold are better), it is used extensively as an electrical conductor. It also has good thermal conductivity, which makes it suitable for thermal management applications. It can be cast and worked easily, because it is quite ductile. One of the major applications of copper in a composite is as a matrix material in niobium-based superconductors. Copper-zinc alloys (brass) and copper-tin alloys (bronze) are solid solution strengthened and among the earliest alloy metals used.

3.4.6 Silver

Silver is another face centered cubic metal. It is a very good electrical and thermal conductor, highly ductile, and has good corrosion resistance. It has found a new use as a matrix material in high temperature oxide superconductors.

3.4.7 Nickel

Nickel is also an FCC metal, which gives it good ductility. More importantly, nickel-based alloys show an excellent combination of properties. Nickel-based superalloys, primarily nickel-iron-cobalt alloys, have superior high-temperature creep resistance, making them suitable for turbine blades.

3.4.8 Niobium

Although niobium alloys are not commonly used as a matrix material in MMCs, they are used as filaments in superconducting composites. We give a brief description of these alloys in Sec. 3.4 below.

3.4.9 Intermetallics

Intermetallics (sometimes referred to as intermetallic compounds) are formed when two dissimilar metals are combined following rules of chemical valence. Generally, the bonding in intermetallics is not metallic, but ionic and covalent in nature. Such an alloy is called an intermetallic compound (Villers and Calvert, 1985; Sauthoff, 1995).

Intermetallics generally have a stoichiometric composition and appear as a line compound in the phase diagram. Some intermetallics have a range of composition. In general, intermetallics have a complex crystal structure and are brittle due to their ionic and covalent bonding. Some intermetallics have been identified to have rather unique attributes of high-temperature strength and stiffness, low density, and excellent oxidation resistance. Used as a matrix material for making composites, they have the potential to increase the operating temperatures over conventional materials.

Intermetallics can have a disordered or ordered structure. Ordered intermetallic alloys possess structures characterized by long-range ordering, i.e., different atoms occupy specific positions in the lattice. Because of their ordered structure, dislocations in intermetallics are much more restricted

than in disordered alloys. This results in retention (and, in some cases, even an increase) in strength at elevated temperatures, a very desirable feature. For example, nickel aluminide shows a marked increase in strength up to 800°C. An undesirable feature of intermetallics is their extremely low ambient temperature ductility.

An important disordered intermetallics is molybdenum disilicide (MoSi₂). It has a high melting point and shows good stability at temperatures greater than 1200° C, in an oxidizing atmosphere. It is commonly used as a heating element in furnaces. The high oxidation resistance comes from a protective SiO₂ film that is formed at high temperatures.

3.5 SUPERCONDUCTIVITY

Since one of the major applications of metal matrix composites is as filamentary superconducting composites, we briefly describe the materials related aspects of the phenomenon of superconductivity.

Certain metals and alloys lose all resistance to the flow of electricity when cooled to within a few degrees of absolute zero. This phenomenon is called superconductivity and the materials exhibiting this phenomenon are called superconductors. Unlike normal metals, these superconductors can carry a high-density current without any electrical resistance. Superconductors can potentially carry as much as 100 times the amount of electricity of ordinary copper or aluminum wires of the same size. This, in turn, can be exploited in devices such as motors and generators, and to transmit electricity in power lines. Superconductors can generate very high magnetic fields that are common in high energy physics and fusion energy programs. Other fields of application include magnetic resonance imaging, magnetohydrodynamic generators, rotating machines, magnetic levitation vehicles, and magnets in general.

Conventional superconductors require cooling in liquid helium (4.2 K), a very costly proposition. In 1986, however, a new class of ceramic superconductors was discovered which exhibited a critical temperature above that of liquid nitrogen (77 K). These are called the high-temperature superconductors and the phenomenon is referred to as high temperature superconductivity (HTS). Unlike the low-temperature superconductors, which are metallic or semimetallic, these new compounds are ceramics. The first HTS discovered had a critical temperature of 35 K (-238° C). Then in 1987, a compound that became superconducting at 94 K (-179° C) was discovered. This discovery was particularly significant because this

compound could be cooled with cheap and readily available liquid nitrogen. This was followed by the discovery of bismuth-based compounds; thalliumand yttrium-based compounds with even higher critical temperature were discovered. The high-temperature superconductors (HTS) can function at temperatures as high as 140 K (-133° C). This allows cooling to be done more economically and efficiently by liquid nitrogen, compared with conventional or low-temperature superconductors which need liquid helium as a cooling medium. In 2001, another low temperature superconductor was discovered with composition MgB₂ (Nagamatsu et al., 2001). Its T_c of 39 K is slightly higher than that of Nb-based metallic superconductors.

Niobium/titanium alloys are one of the important low-temperature superconductors. Low-temperature superconductors must be cooled to below 20 K in order to become superconducting. They are widely used in magnetic resonance imaging (MRI) machines, and in the fields of high-energy physics and nuclear fusion. Additional commercial use has been limited largely by the high refrigeration costs associated with liquid helium, which is needed to cool the materials to such low temperatures.

3.5.1 Types of Superconductors

The phenomenon of superconductivity was discovered in mercury by Onnes in 1911. Since then, many 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 3.6 shows the variation of electrical resistivity with temperature of a normal metal and that of a superconducting material. T_c is the critical temperature, a characteristic constant of each material, above which the material becomes a normal conductor. Kunzler et al. (1961) discovered the high critical field capability of Nb₃Sn and thus opened up the field of practical, high-field superconducting magnets. 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.

The technologically most important property of superconductors is their capacity to carry an electric current without normal I^2R (I is the current in amp and R is the resistance in ohm) losses up to a critical current density, J_c . This critical current is a function of the applied field and temperature. The



Fig.3.6 Variation of electrical resistivity with temperature for a normal metal and that of a superconducting material.

commercially available superconductors in the 1980s could demonstrate critical current densities of $J_c > 10^6$ A cm⁻² at 4.2 K and an applied field of H = 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. 3.7. As long as the material does not cross into the shaded area indicated in Fig. 3.7, it will behave as a superconductor.

There are two types of superconductors:

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_{c2} . 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 its normal state. All major applications of superconductivity involve the use of type II superconductors.

3.5.2 Flux and Flux-Pinning

When magnetic lines of force from a strong magnetic field, called flux lines,



Fig. 3.7 The state of superconductivity is described by three critical parameters: magnetic field (H), temperature (T), and current density (J). As long as the material does not cross into the shaded area, it will behave as a superconductor.

try to penetrate the surface of a Type 2 superconductor, we get what is called a flux-lattice. This periodic lattice, consisting of tubular regions of flux lines, stems from the tiny magnetic moments in each flux line, which repel each other and array themselves in an orderly fashion, usually in the close packed hexagonal arrangement. Flux pinning is required in superconductors because movement of flux, sometimes called "flux-creep," is an energy-dissipative process; that is, heat is produced. Any disturbance of a superconductor, say, by motion or a change in the applied field, leads to a rearrangement of magnetic flux lines in the superconductor. Flux movement in a superconductor, irrespective of the source of flux movement, results in a temperature increase. This leads to a reduced critical current and more flux movement. The net result is that the superconductor is heated above T_c and reverts to its 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. 3.8. Flux-pinning occurs via defects in the crystalline structure of the superconductor such as grain boundaries or impurities. The



Fig. 3.8 The cryostabilization design concept: fine filaments reduce the energy dissipated due to magnetic flux movement.

high-purity copper or silver 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 matrix and a coolant is in contact with all windings.

3.5.3 Ductile Alloys: 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 in the United Kingdom, Nb-46.5% Ti in the United States, and Nb 50% Ti in Germany. Figure 3.9 shows the Nb-Ti phase diagram as well as the critical temperature and upper critical field as a



Fig. 3.9 The top figure shows the Nb-Ti phase diagram while the bottom figure shows the critical temperature and upper critical field as a function of alloy composition. Note the range (46-50 wt.% Ti) for the superconducting alloys. (after Hillmann, 1981).

function of alloy composition. Note the range (46-50 wt.% Ti) for the superconducting alloys.

In all these alloys, a $J_c > 1000$ A mm² 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 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. As pointed out above, 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 becomes important in high-Ti alloys because the Nb-Ti phase diagram indicates precipitation of α -Ti in these alloys. As pointed out above, 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.

3.5.4 A-15 Superconductors: Nb₃Sn

For applications involving fields greater than 12 T, the ordered intermetallic compounds having an A-15 crystal structure are better suited than the Nb-Ti type. Nb₃Sn has a T_c of 18 K. It is easy to appreciate that the higher the T_c, the lower the refrigeration costs. Nb₃Sn is the most widely used superconductor for high fields and high temperatures. A characteristic feature of these intermetallic compounds is their extreme brittleness (typically, a strain-to-failure of 0.2% with very little plasticity). Compare this to Nb-Ti which can be cold worked to a reduction in area over 90%. Initially, the compound Nb₃Sn 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. V₃Ga on a vanadium ribbon was also produced in this manner. The main disadvantages of these ribbon type superconductors were: (a) flux instabilities due to one wide dimension in the ribbon geometry and (b) limited flexibility in the ribbon width direction. Later on, 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 V₃Ga could be produced on vanadium filaments in a Cu-Ga matrix while Kaufmann and Pickett (1970) demonstrated that Nb₃Sn could

be obtained on niobium filaments from a bronze (Cu-Sn) matrix. The processing of some important superconducting composite systems is described in chapter 4, while their applications are given in chapter 11.

References

- Chawla, N., J.J. Williams, and R. Saha, (2002) Metall. Mater. Trans., 33A, 3861.
- Ganesh, V.V., and N. Chawla, (2004) Metall. Mater. Trans., 35A, 53-62.
- Hillmann, H., (1981) in *Superconductor Materials Science*, Plenum, New York, p. 275.
- Kaufmann, A.R., and J.J. Pickett, (1970) Bull. Am. Phys. Soc., 15, 833.
- Kunzler, J.E., E. Bachler, F.S.L. Hsu, and J.E. Wernick, (1961) Phys. Rev. Lett., 6, 89.
- Meyers, M.A., and K.K. Chawla, (2005) *Mechanical Behavior of Materials*, 2nd edition, Prentice Hall, Upper Saddle River, NJ.
- Nagamatsu, J., N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, (2001) *Nature*, **410**, 63.
- Sauthoff, G., (1995) Intermetallics, VCH Publishers, New York, NY.
- Smithells Metals Reference Book, (1976) Butterworths, Boston, p. 944.
- Tachikawa, K., (1970) in *Proceedings of the 3rd ICEC*, Illife Science and Technology Publishing, Surrey, U.K.
- Pearson's Handbook of Crystallographic Data for Intermetallic Phases, (1985), vol. 1,2,3, P. Villers and L.D. Calvert (eds.), ASM, Metals Park, OH.