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## CHAPTER I.2.3 METALS: BASIC PRINCIPLES

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### INTRODUCTION

Since large segments of the medical device industry rely on implants with one or more metallic parts – e.g., stents, heart valves, orthopedic hips and knees, plus oral/maxillofacial implants – metals have a highly significant place in the biomaterials market. In view of this wide utilization of metallic biomaterials, this chapter provides some basic principles underlying the quantification and design-related manipulation of composition, structure, and properties of metallic biomaterials. Major themes are the metallurgical principles underlying structure–property relationships, and the larger problem of design, production, and proper utilization of medical devices.

### STEPS IN THE FABRICATION OF METALLIC BIOMATERIALS

Understanding the structure and properties of metallic implant materials requires an appreciation of the metallurgical significance of the material's processing history. Typically, any metallic medical device will differ in exactly how it is manufactured, so it is useful to look briefly at some generic processing steps in implant manufacture (Figure I.2.3.1A).

#### Metal-Containing Ore to Raw Metal Product

With the exception of noble metals such as gold (which do not represent a major fraction of implant metals),

metals exist in the Earth's crust in mineral form, wherein the metal is chemically combined with other elements, as in the case of metal oxides. These mineral deposits, or “ore,” must be located, mined, separated, and enriched for further processing into pure metal or various alloys. For example, in the case of titanium, certain mines in the southeastern United States yield sands containing common quartz along with mineral deposits of zircon, titanium, iron, and rare earth elements. The sandy mixture can be concentrated by using water flow and gravity to isolate titanium-containing compounds such as rutile ( $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_3$ ). To obtain rutile, which is particularly good for making metallic titanium, further processing typically involves electrostatic separations. Then, to extract titanium metal from the rutile, one method involves treating the ore with chlorine to make titanium tetrachloride liquid, which in turn is treated with magnesium or sodium to produce chlorides of the latter metals along with bulk titanium “sponge” according to the Kroll process. At this stage, the titanium sponge is not of controlled purity, so depending on the purity (“grade”) of the final titanium product that is sought, it is necessary to refine it further by using vacuum furnaces, remelting, and additional steps. All of this is critical in producing titanium with the appropriate properties, as exemplified in the production of the most common grades of commercially pure (CP) titanium; these grades differ in oxygen content by only tenths of a percent, yet these small differences in oxygen content make major differences in mechanical properties, including yield, tensile and fatigue strength of titanium.

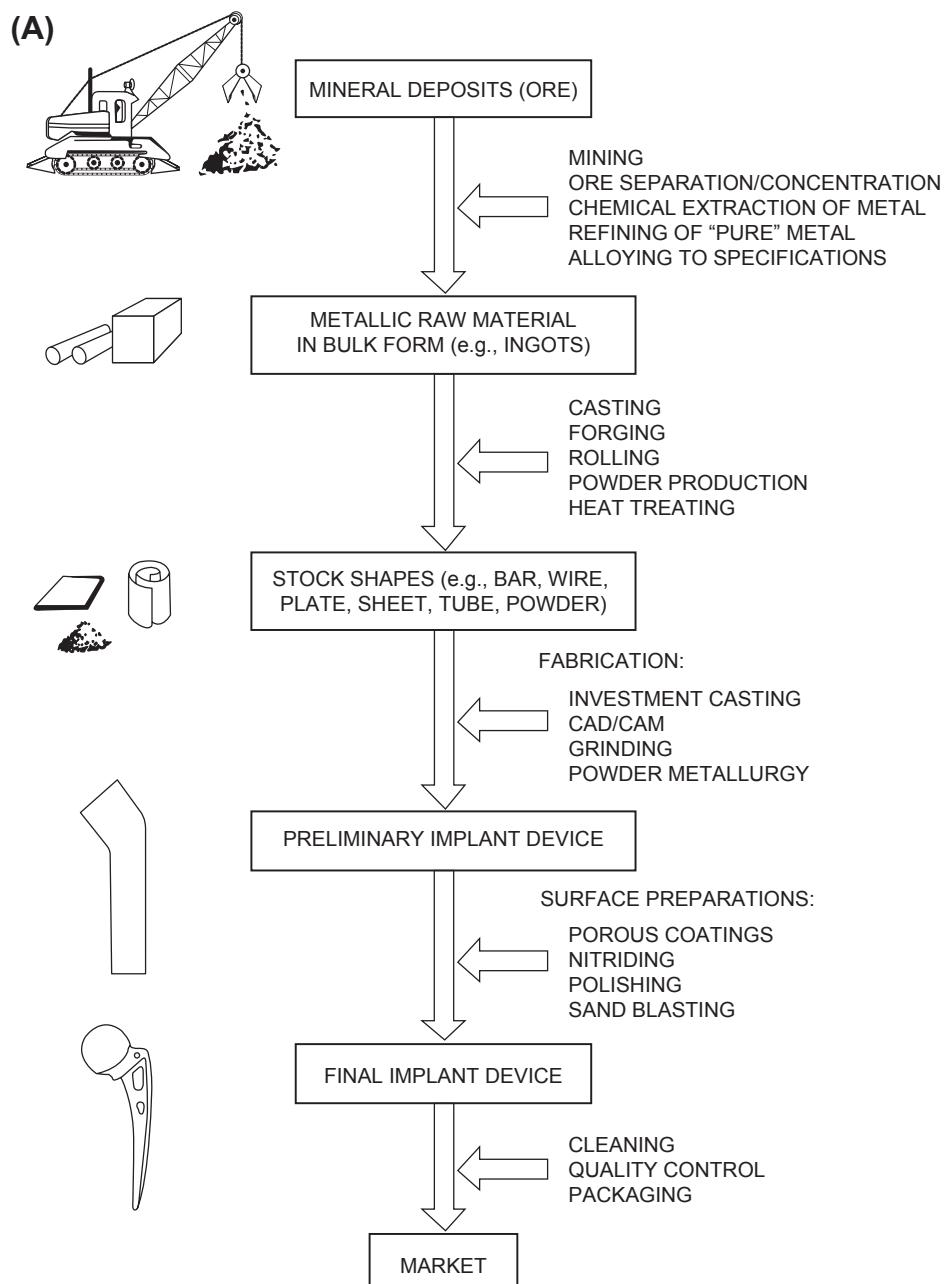
After extraction steps, the resulting raw metal product eventually emerges in some type of bulk form, such as ingots, which can be supplied to raw materials' vendors or metal manufacturers. For instance, in the case of multicomponent metallic implant alloys (i.e., made up of more than one element), the raw metal product will usually have to be further processed both chemically

and physically. Processing steps can include remelting, addition of specific alloying elements, and controlled solidification from the melt, in order to produce an alloy that meets certain chemical and metallurgical specifications. For example, to make ASTM (American Society for Testing and Materials) F138 316L stainless steel, iron is alloyed with specific amounts of carbon, silicon, nickel, and chromium; and to make ASTM F75 or F90 alloy, cobalt is alloyed with specific amounts of chromium, molybdenum, carbon, nickel, and other elements. Table I.2.3.1 lists ASTM designations and typical properties of common metallic alloys for surgical implants.

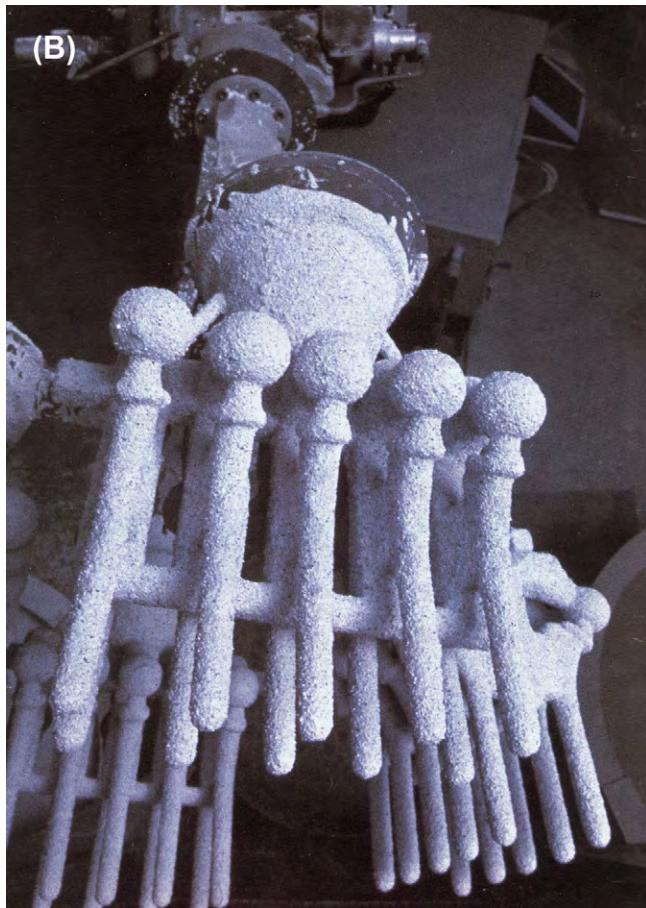
## Raw Metal Product to Stock Metal Shapes

A metal supplier will typically further process the bulk raw metal product (metal or alloy) into stock bulk shapes, such as bars, wire, sheet, rods, plates, tubes or powders. These stock shapes may then be sold to implant manufacturers, who typically want a stock shape that is closer to the final implant shape, e.g., a maker of screw-shaped dental implants would often buy rod stock of the appropriate metal as feedstock for screw-manufacturing machines.

A metal supplier might transform the raw metal product into stock shapes by a variety of processes, including



**FIGURE I.2.3.1** (A) Generic processing history of a typical metallic implant device, in this case a hip implant.



**FIGURE I.2.3.1** (B) Image of one step during the investment casting (“lost wax”) process of manufacturing hip stems; a rack of hip stems can be seen attached to a system of sprues through which molten metal can flow. At this point, ceramic investment material composes the mold into which the molten metal will flow and solidify during casting, thereby replicating the intended shape of a hip stem.

remelting and continuous casting, hot rolling, forging, cold drawing through dies, etc. Depending on the metal there might also be heat-treating steps (i.e., carefully controlled heating and cooling cycles) designed to: facilitate further working or shaping of the stock; relieve the effects of prior plastic deformation (e.g., as in annealing) or produce a specific microstructure and properties in the stock material. Because of the high chemical reactivity of some metals at elevated temperatures, high temperature processing may require vacuum conditions or inert atmospheres to prevent unwanted uptake of oxygen by the metal, all of which can add to the cost of production. For instance, in the production of fine powders of ASTM F75 Co-Cr-Mo alloy, molten metal is ejected through a small nozzle to produce a fine spray of atomized metal droplets that solidify while cooling in an inert argon atmosphere.

Typically, stock shapes are chemically and metallurgically tested at this early stage to ensure that the chemical composition and microstructure of the metal sold to an implant company conforms to industry standards for surgical implants (e.g., ASTM Standards), as discussed

later in this chapter. It makes sense that an implant manufacturer will demand quality assurance that they are buying an appropriate grade of metal from the supplier of the raw metal stock.

### Stock Metal Shapes to Preliminary and Final Metal Devices

Typically, an implant manufacturer will buy stock material and then fabricate preliminary and final forms of the device. Specific steps depend on a number of factors, including the final geometry of the implant, the forming and machining properties of the metal, and the costs of alternative fabrication methods. Typical fabrication methods include investment casting (the “lost wax” process), conventional and computer-based machining (CAD/CAM), forging, powder metallurgical processes (e.g., hot isostatic pressing or HIP), and a range of grinding and polishing steps. A variety of fabrication methods are required because not all implant alloys can be feasibly or economically fabricated into a final form in the same way. As one example, cobalt-based alloys are extremely difficult to machine into the complicated shapes of some implants by conventional machining methods. Therefore, many cobalt-based alloys are frequently shaped into implant forms by investment casting (e.g., **Figure I.2.3.1B**) or by powder metallurgy. On the other hand, titanium is relatively difficult to cast, and is therefore often machined.

Other aspects of fabrication (which to some degree more accurately fall under the heading of surface treatment) involve the application of macro-, micro-, and/or nano-level coatings on implants, often with the intent of producing certain ranges of surface roughness. Such surface modifications have become more popular in recent years as a means to improve fixation of implants in bone or to improve interfacial bone growth. The surface coating or roughening can take various forms, and can require different fabrication technologies. In some cases, modifications to the surface have the potential to negatively affect the metallurgical properties of the underlying bulk implant metal. For example, in the case of alloy beads or “fiber metal” coatings for macro-porous implants, the manufacturer may employ high temperature sintering to apply the coating over specific regions of the implant surface (e.g., on the proximal portion of a femoral hip stem). Sintering involves heating the coating and substrate to about half (or more) of the alloy’s melting temperature in order to encourage diffusion, which in turn helps form the necks that join the beads to one another and to the implant’s surface. Such reasonably high temperatures can modify the underlying metallic substrate by allowing grain growth or other mechanisms, which could negatively affect the properties. An alternative to sintering is plasma or flame spraying a metal onto an implant’s surface. In this process, hot, high velocity gas plasma is charged with a metallic powder and directed at appropriate regions of

**TABLE I.2.3.1 | Typical Mechanical Properties of Implant Metals<sup>a</sup>**

Material	ASTM Designation	Condition	Young's Modulus (GPa)	Yield Strength (MPa)	Tensile Strength (MPa)	Fatigue Endurance Limit Strength (at 10 <sup>7</sup> cycles, R = -1 <sup>c</sup> ) (MPa)
Stainless steel	F745 F55, F56, F138, F139	Annealed	190	221	483	221–280
		Annealed	190	331	586	241–276
	F745 F55, F56, F138, F139	30% Cold-worked	190	792	930	310–448
		Cold forged	190	1213	1351	820
Co-Cr alloys	F75	As-cast/annealed	210	448–517	655–889	207–310
		P/M HIP <sup>b</sup>	253	841	1277	725–950
	F799	Hot forged	210	896–1200	1399–1586	600–896
		Annealed	210	448–648	951–1220	Not available
	F90	44% Cold-worked	210	1606	1896	586
		Hot forged	232	965–1000	1206	500
		Cold-worked, aged	232	1500	1795	689–793 (axial tension R = 0.05, 30 Hz)
Ti alloys	F67	30% Cold-worked Grade 4	110	485	760	300
		Forged annealed	116	896	965	620
	F136	Forged, heat treated	116	1034	1103	620–689

<sup>a</sup> Data collected from references noted at the end of this chapter, especially Table 1 in Davidson and Georgette (1986).

<sup>b</sup> P/M HIP: Powder metallurgy product, hot-isostatically pressed.

<sup>c</sup> R is defined as  $\sigma_{\min}/\sigma_{\max}$ .

an implant surface. The powder particles fully or partially melt, and then fall onto the substrate surface, where they solidify rapidly to form a tough coating. This has the advantage of not excessively heating the substrate.

Still more surface treatments are available, including ion implantation (to produce better surface properties), nitriding, and coating with a thin diamond film. For example, in nitriding, a high energy beam of nitrogen ions is directed at the implant under vacuum so that nitrogen atoms penetrate the surface and come to rest at sites in the substrate. Depending on the alloy, this process can produce enhanced properties, such as improved surface hardness and wear properties. (Many examples of different levels of surface modifications – ranging from the nano-level up to the macro level – can be seen by perusing the advertisements for oral and maxillofacial implants in any one of the many journals devoted to such implants.)

Finally, a manufacturer of a metallic implant device will normally perform a set of finishing steps. These vary with the metal and manufacturer, but typically include chemical cleaning and passivation (i.e., rendering the metal inactive if exposed to a corrosive environment). Electrolytically-controlled treatments may also be used to remove machining chips or impurities that may have become embedded in the implant's surface. As a rule, these steps are conducted according to good manufacturing practice (GMP), and ASTM specifications for cleaning and finishing implants. Notably, these finishing steps can be extremely important to the overall biological performance of the implant because they can affect the detailed surface properties of the medical device – which

govern the surface of the device that comes in direct contact with the blood and other tissues at the implant site.

## MICROSTRUCTURES AND PROPERTIES OF IMPLANT METALS

In order to understand the properties of each alloy system in terms of microstructure and processing history, it is essential to know: (1) the chemical and crystallographic identities of the phases present in the microstructure; (2) the relative amounts, distribution, and orientation of these phases; and (3) the effects of the phases on properties. This section of the chapter emphasizes mechanical properties of metals used in implant devices, even though other properties, such as surface properties and wear properties, must also be considered and may in some instances be more critical to control. (Surface properties of materials are reviewed in more depth in Chapter I.1.5 of this textbook.) The basic principles are illustrated here in the context as applied to the stainless steels, cobalt-based alloys, and titanium-based alloys – which are very commonly used in medical devices. (More detailed discussions follow in the separate chapters in this textbook on stainless steel (Chapter I.2.3.B) and titanium (Chapter I.2.3.A).)

### Microstructure and Mechanical Properties

There are many ways to manipulate microstructures and properties of metallic biomaterials. The following sections highlight just a few of the more commonly-encountered principles that apply to the most common

metallic biomaterials, including the stainless steels, Co-Based alloys, and Ti-based alloys.

**316L Stainless Steel.** In this alloy, two common strengthening methods are cold-working and controlling grain size. The basis of each method is the idea of increasing the difficulty of slip of dislocations. In cold-working, the idea is to introduce more and more plastic deformation such that additional plastic flow becomes even more difficult. In decreasing grain size, the idea is to have more grain boundaries to interfere with the flow of dislocations on slip systems within each grain.

With 316L stainless (ASTM F138), typically it is used in a 30% cold-worked state, because this cold-worked metal has a markedly increased yield, ultimate tensile, and fatigue strength relative to the annealed state (Table I.2.3.1). The trade-off in this case is decreased ductility of the cold-worked metal, but ordinarily this is not a major concern in implant products. In dealing with grain size in 316L, the recommended grain size is ASTM #6 or finer, in which the grain size number  $n$  is defined in the formula  $N = 2^{n-1}$ , where  $N$  is the number of grains counted in a 1 in<sup>2</sup> area at 100 × magnification (0.0645 mm<sup>2</sup> actual area). As an example, when  $n = 6$ , the grain size is about 100 micrometers. The emphasis on a fine grain size is explained by the well-known Hall-Petch-type relationship (Hall, 1951; Petch, 1953), which relates mechanical yield stress and grain diameter as follows:

$$t_y = t_i + kd^{-m}$$

where  $t_y$  and  $t_i$  are the yield and friction stress, respectively;  $d$  is the grain diameter;  $k$  is a constant associated with propagation of deformation across grain boundaries; and  $m$  is approximately 0.5. This equation indicates that a higher yield stress may be achieved by a metal with a smaller grain diameter  $d$ , all other things being equal. A key determinant of grain size is manufacturing history, including details on solidification conditions, cold-working, annealing cycles, and recrystallization.

**Cobalt-Based Alloys.** Cobalt-based alloys include Haynes-Stellite 21 and 25 (ASTM F75 and F90, respectively), forged Co-Cr-Mo alloy (ASTM F799), and multiphase (MP) alloy MP35N (ASTM F562). The F75 and F799 alloys are virtually identical in composition, each being about 58–70% Co and 26–30% Cr, with the key difference in their processing history. The other two alloys, F90 and F562, have slightly less Co and Cr, but more Ni (F562) or more tungsten (F90).

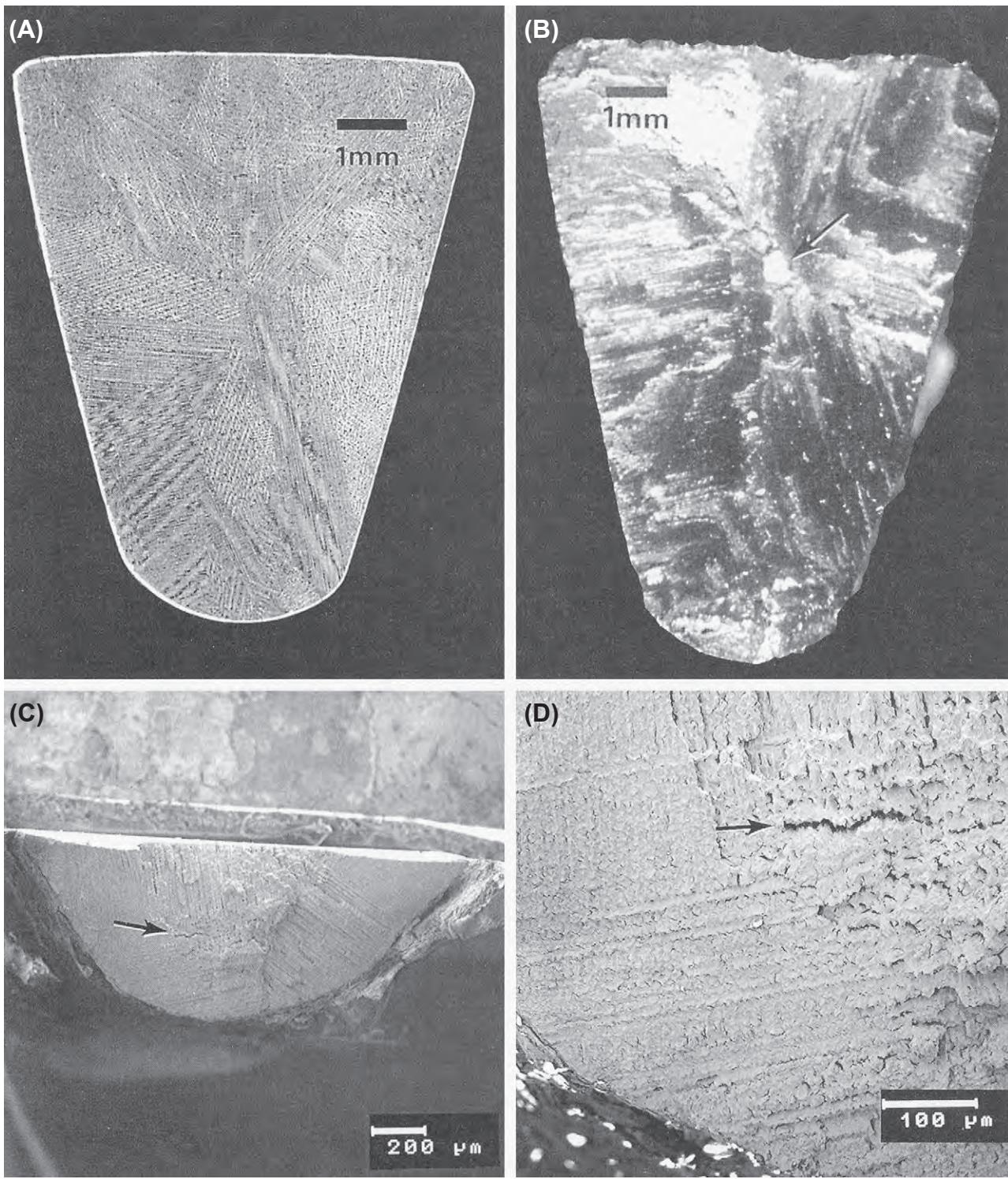
To consider the example of F75 alloy (which has a long history in both the aerospace and biomedical implant industries), the main attribute of this alloy is corrosion resistance in chloride environments, which is related to its bulk composition and surface oxide (nominally Cr<sub>2</sub>O<sub>3</sub>). When F75 is cast into shape by investment casting (e.g., the “lost wax” process; Figure I.2.3.1B), the alloy is first melted at 1350–1450°C and then poured or pressurized into ceramic molds of the desired shape (e.g., femoral stems for artificial hips, oral implants, dental

partial bridgework). The sometimes intricately-shaped molds are made by fabricating a wax pattern to near-final dimensions of the implant and then coating (or “investing”) the pattern with a special ceramic, which then holds its shape after the wax is burned out prior to casting – hence the name “lost wax” for the process. Molten metal is poured into the ceramic mold through sprues, or pathways, and then, once the metal has solidified into the shape of the mold, the ceramic mold is cracked away and processing of the metal continues toward the final device.

Depending on the exact details of the casting process, at least three microstructural features can come into play as strong determinants of implant properties. First, as-cast F75 alloy typically consists of a Co-rich matrix (alpha phase) plus interdendritic and grain boundary carbides (primarily M<sub>23</sub>C<sub>6</sub>, where M represents Co, Cr or Mo). Overall, the relative amounts of the alpha and carbide phases should be approximately 85% and 15%, respectively, but due to non-equilibrium cooling, it is possible that a “cored” microstructure may develop. In this situation, the interdendritic regions become rich in solute (Cr, Mo, C) and contain carbides, while the dendrites become depleted in Cr and richer in Co. This creates an unfavorable electrochemical situation, with the Cr-depleted regions being anodic with respect to the rest of the microstructure. (This is also an unfavorable situation if a porous coating will subsequently be applied by sintering to this bulk metal.) Subsequent solution-annealing heat treatments at 1225°C for 1 hour can help alleviate this situation.

A second issue with F75 solidification is that dendrites will form, along with a relatively large grain size. This is generally undesirable because it decreases the yield strength via a Hall-Petch relationship between yield strength and grain diameter (recall the discussion from the section on stainless steel above). An example of dendritic growth and large grain diameter (approximately 4 mm) can be easily seen in Figures I.2.3.2A and I.2.3.2B, which show metallographic cross-sectional views through a femoral hip stem, and also a dental implant (Figures I.2.3.2C, I.2.3.2D) manufactured by investment casting.

A third issue with cast F75 is that casting defects may arise, e.g., Figure I.2.3.2B shows an inclusion in the middle of the cross-section through the distal third of the femoral hip stem. The inclusion was a particle of the ceramic mold (investment) material, which presumably broke off and became trapped within the interior of the mold while the metal was solidifying. This contributed to a fatigue fracture of the implant device *in vivo*, most likely because of stress concentrations and crack initiation sites associated with the ceramic inclusion. For similar reasons, it is also desirable to avoid macro- and microporosity arising from metal shrinkage upon solidification of castings. As an example of such porosity, Figures I.2.3.2C and I.2.3.2D exemplify a markedly dendritic microstructure with large grain size and



**FIGURE I.2.3.2** (A) Macrophoto of a metallographically polished and etched cross-section of a cast Co–Cr–Mo ASTM F75 femoral hip stem, showing dendritic structure and large grain size. (B) Macrophoto of the fracture surface of the same Co–Cr–Mo ASTM F75 hip stem as in (A). Arrow indicates large inclusion within the central region of the cross section. Fracture of this hip stem occurred *in vivo*. (C), (D) Scanning electron micrographs of the fracture surface from a cast F75 subperiosteal dental implant. Note the large grain size, dendritic microstructure, and interdendritic microporosity (arrows).

microporosity at the fracture surface of a dental implant fabricated by investment casting.

To avoid problems such as the ones described above with cast F75, powder metallurgical techniques have been designed and used by some implant manufacturers.

For example, in hot isostatic pressing (HIP), a fine powder of F75 alloy is compacted and sintered together under appropriate pressure and temperature conditions (about 100 MPa at 1100°C for 1 hour) and then forged to final shape. The typical microstructure shows a much smaller

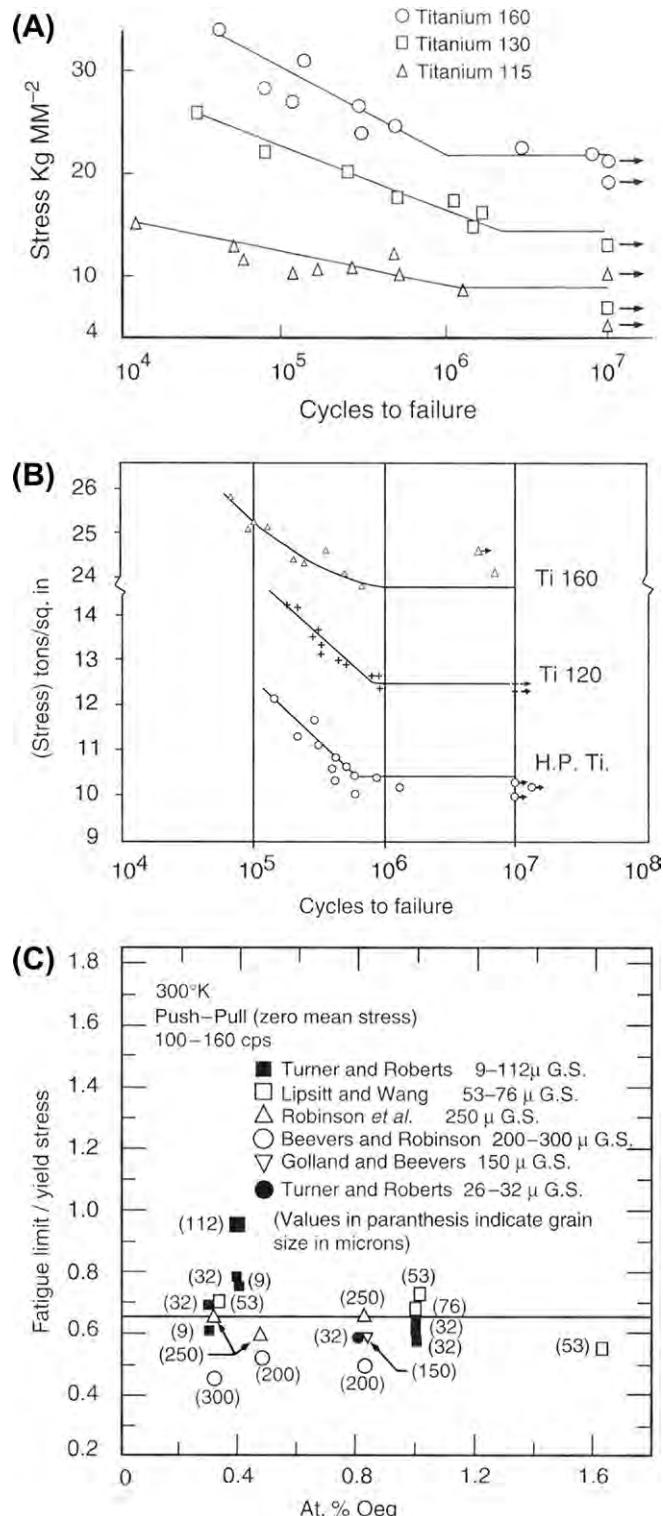
grain size than with casting (e.g., about 8 microns), which has the benefit of a much higher yield strength (via the Hall-Petch relationship), and better ultimate and fatigue properties than the as-cast alloy (Table I.2.3.1).

One final example with F75 alloy is the issue of porous-coated implants made by sintering. Here the idea is to sinter (join) the beads together, and to the underlying bulk substrate. With Co-based alloys like F75, however, sintering can be difficult, requiring temperatures near the melting point ( $1225^{\circ}\text{C}$ ), which in turn can decrease the fatigue strength of the substrate alloy. For example, cast/solution-treated F75 alloy has a fatigue strength of about 200–250 MPa, but this strength can decrease to about 150 MPa after porous coating treatments – evidently from further phase changes in the non-equilibrium cored microstructure in the original cast F75 alloy. On the other hand, it has been found that a modified sintering treatment can return the fatigue strength back up to about 200 MPa (Table I.2.3.1).

**Titanium-Based Alloys.** Commercially pure (CP) titanium (ASTM F67) and extra-low interstitial (ELI) Ti-6Al-4V alloy (ASTM F136) are the two most common titanium-based implant biomaterials (although within the category of CP Ti there are four grades). F67 CP Ti is 98.9–99.6% Ti. The oxygen content of CP Ti, as well as the content of other interstitial elements (e.g., C and N), affect its yield, tensile, and fatigue strengths significantly. With Ti-6Al-4V ELI alloy, the individual Ti-Al and Ti-V phase diagrams suggest the effects of the alloying additions in the ternary alloy; since Al is an alpha (HCP) phase stabilizer and V is a beta (BCC) phase stabilizer, Ti-6Al-4V alloy used for implants is an alpha-beta alloy.

For CP titanium implants (as exemplified by many current dental implants) typical microstructures are made up of single-phase alpha titanium (having the HCP structure), in which there is typically mild (30%) cold-work and grain diameters in the range of 10–150 microns, depending on manufacturing. The nominal mechanical properties are listed in Table I.2.3.1. Beyond cold-work, interstitial elements (O, C, N) in both CP titanium and the Ti-6Al-4V alloy strengthen the metal through interstitial solid solution strengthening mechanisms, with nitrogen having approximately twice the hardening effect (per atom) of either carbon or oxygen. As noted earlier, the oxygen content of CP Ti (and the interstitial content generally) affects its yield, tensile, and fatigue strengths significantly. For example, data available in the ASTM standard show that at 0.18% oxygen (grade 1), the yield strength is about 170 MPa, whereas at 0.40% (grade 4) the yield strength is about 485 MPa.

Likewise, the ASTM standard shows that the tensile strength increases with oxygen content. The literature also reveals that the fatigue limit of unalloyed CP Ti is typically increased by interstitial content, in particular the oxygen content. For example, Figure I.2.3.3A shows data from Beevers and Robinson (1969), who tested



**FIGURE I.2.3.3** (A) S-N curves (stress amplitude-number of cycles to failure) at room temperature for CP Ti with varying oxygen content (see text for O content of Ti 160, 130, and 115), from Beevers and Robinson (1969). (B) S-N curves at room temperature for CP Ti with varying oxygen content (see text), from Turner and Roberts (1968a). (C) Ratio of fatigue limit to yield stress in unalloyed Ti at  $300^{\circ}\text{K}$  as a function of at% oxygen and grain size, from Conrad et al. (1973). See Bibliography for details of references given within this figure.

vacuum-annealed CP Ti having a grain size in the range 200–300 microns in tension-compression at a mean stress of zero, at 100 cycles/sec. The  $10^7$  cycle endurance limit, or fatigue limit, for Ti 115 (0.085 wt% O, grade 1), Ti 130 (0.125 wt% O, grade 1), and Ti 160 (0.27 wt% O, grade 3) was 88.3, 142, and 216 MPa, respectively. Figure I.2.3.3B shows similar results from Turner and Roberts' (1968a) fatigue study on CP Ti (tension-compression, 160 cycles/sec, mean stress equals zero) having a grain size in the range 26–32 micrometers. Here the fatigue limit for "HP Ti" (0.072 wt% O, grade 1), Ti 120 (0.087 wt% O, grade 1), and Ti 160 (0.32 wt% O, grade 3) was 142, 172, and 295 MPa, respectively – again showing an increasing endurance limit with increasing oxygen content. Also, for grade 4 Ti in the cold-worked state, Steinemann et al. (1993) reported a  $10^7$  endurance limit of 430 MPa. Other workers (Conrad et al., 1973) have reported fatigue studies on CP Ti at 300°K, and noted that the ratio of fatigue limit to yield stress is relatively constant at about 0.65, independent of interstitial content and grain size (Figure I.2.3.3C). The work of Turner and Roberts also reported that the ratio  $f$  (defined as fatigue limit/ultimate tensile strength) – also referred to as the "fatigue ratio" in materials design textbooks (e.g., see Charles and Crane, 1989, p. 106) – was 0.43 for the high-purity Ti (0.072 wt% O), 0.5 for Ti 120 (0.087 wt% O), and 0.53 for Ti 160 (0.32 wt% O). It seems clear that interstitial content affects the yield and tensile and fatigue strengths in CP Ti.

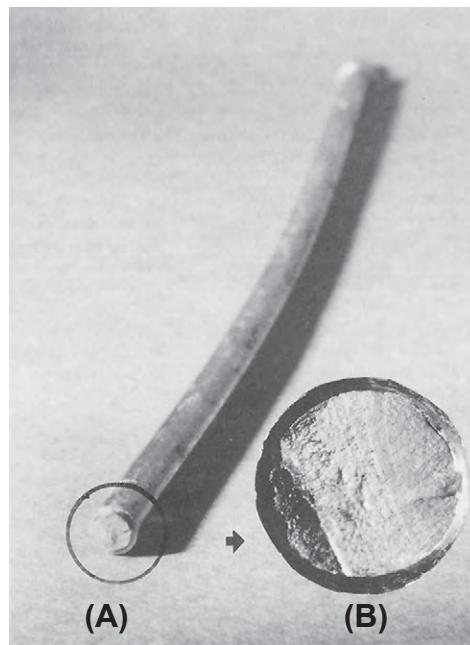
At the same time, cold-work appears to increase the fatigue properties of CP Ti. For example, Disegi (1990) quoted bending fatigue data for annealed versus cold-worked CP Ti in the form of un-notched 1.0 mm thick sheet, and showed a moderate increase in ultimate tensile strength (UTS) and "plane bending fatigue strength," when comparing annealed versus cold-rolled Ti samples. Based on these data, the ratio of fatigue strength to ultimate tensile strength ("endurance ratio" or "fatigue ratio," see paragraph above) varied between 0.45 and 0.66. On the other hand, the *ASM Handbook Fatigue and Fracture* (Wagner et al., 1996) noted that the fatigue limit for high purity Ti only increased about 10% relative to the annealed material, while Disegi's data showed that the fatigue strength increased by about 28%, on average, with cold-work.

## CONCLUDING REMARKS

Metallurgical structure–property relationships inform materials selection in medical implant design, just as they do in the design of any well-engineered product. Although this chapter's emphasis has been on mechanical properties (for the sake of specificity), other properties – including surface properties – are receiving increasing attention in relation to biological performance of implants. Examples of this latter theme are efforts to

attach relevant biomolecules to metallic implant surfaces to promote certain desired interfacial activities, and attempts to develop special surface textures on implants to guide molecular and cellular reactions; these subjects can be researched further based on the following Bibliography.

Another point to remember is that the intrinsic material properties of metallic implants – e.g., Young's elastic modulus, yield strength, or fatigue strength – are not the sole determinant of implant performance and success; overall implant design is also critical. So while it is certainly true that inadequate attention to intrinsic material properties can doom a device to failure, it is also true that even with the best intrinsic properties, a device may still fail because of faulty structural properties, inappropriate use of the implant, surgical error or overall inadequate mechanical design of the implant. As an illustration of this latter point, Figure I.2.3.4 shows a plastically-deformed 316L stainless steel Harrington spinal distraction rod (*circa* 1980s) that failed *in vivo* because of metallurgical fatigue. A failure analysis of this case concluded that failure did not occur because of any shortcomings in the rod's 316L cold-worked stainless steel; rather, the fracture occurred because of a combination of other factors, namely: (1) the surgeon plastically bent the rod to make it fit a bit better in the patient's back (and the rod company sold rod-bending jigs!), but



**FIGURE I.2.3.4** The smooth part of a 316L stainless steel Harrington spinal distraction rod that fractured by fatigue *in vivo*. Note the bend in the rod (the rod was originally straight) and (insert) the relationship of the crack initiation zone of the fracture surface to the bend. The inserted photo shows the nature of the fatigue fracture surface, which is characterized by a region of "beach marks" and a region of sudden overload failure. (Photo courtesy of Bruski, J. B., Hill, D. C. & Moskowitz, A. (1983). Stresses in a Harrington distraction rod: Their origin and relationship to fatigue fractures *in vivo*. *J. Biomech. Eng.*, 105, 101–107.)

the bend in the rod increased the bending moment and bending stresses on the rod at the first ratchet junction, which was a known problem area in terms of fractures *in vivo*; (2) the stress concentrations at the fracture site at the ratchet end of the rod were severe enough to significantly increase the tensile stresses at the first ratchet junction, which was the eventual site of the fatigue fracture; and (3) spinal fusion did not occur in the patient, which contributed to relatively persistent loading of the rod over several months post-implantation, thus further predisposing the implant to fatigue fracture. Here the point is that all three of these factors could have been anticipated and considered in the original design of the rod, during which both structural and material properties could have been considered in various stress analyses to forestall fatigue failure. While this example comes from spinal implants, there are many similar examples with the same theme in the orthopedic, oral, and maxillofacial areas. The take-home message here is that implant design is generally a multifaceted problem in which biomaterials selection is only a part of the overall design problem.

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## A. TITANIUM AND NITINOL (NiTi)

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Titanium and its alloys have attracted much attention in the medical implants field, not only because of their unique mechanical properties and resistance to corrosion, they do not initiate an allergenic response and have the probably the best tolerance among metallic biomaterials in the body. Currently only three alloy systems have extensive use in the industry, specifically commercially pure titanium (cpTi), Ti-6Al-4V, and Ti-6A1-7Nb. These alloy systems represent a very significant percentage of the market for titanium biomaterials.

In its elemental form, titanium has a hexagonal closed packed crystal structure (hcp), named  $\alpha$ , up to a temperature of 882.5°C, where it transforms into a body centered cubic structure (bcc), named  $\beta$ , up to its high melting point temperature at 1668°C (Collings, 1994). Due to this allotropic change, and depending on the alloying elements, titanium alloys are classified as  $\alpha$ , near- $\alpha$ ,  $\alpha + \beta$ , metastable  $\beta$ , or stable  $\beta$ , depending on the phase and microstructure stabilized at room temperature (Polmear, 1981). Alloying elements are classified as  $\alpha$ -stabilizers, such as Al, O, N, C;  $\beta$ -stabilizers, such as Mo, V, Nb, Ta, Fe, W, Cr, Si, Co, Mn, H; and neutral, such as Zr.  $\alpha$  and near  $\alpha$  alloys exhibit superior corrosion resistance, but find limited applications as biomaterials due to their low room temperature strength. The  $\alpha + \beta$  alloys exhibit higher strength (with an elastic modulus around 110 GPa) due to the combination of both phases, whereas the  $\beta$  alloys exhibit a unique combination of low elastic modulus (Young's modulus around 60 GPa) and superior corrosion resistance (Bania, 1993; Schutz, 1993). The final properties of the alloy depend on the chemical composition which affects the  $\alpha$  and  $\beta$  phase relative proportions that can be modified by thermal treatment, and thermo-mechanical processing conditions.

## FABRICATION

Ti and Ti alloys are fabricated into semi-finished bulk products by conventional plastic forming methods, such as forging, rolling, pressing, and drawing. Most Ti materials are processed to avoid an excessive intake of O, N, and H during heating and annealing, since these interstitial elements may induce embrittlement. The hot-working temperature for fabrication has to be carefully selected, since this depends on the alloy composition, and has to be controlled in order to obtain the desired mechanical properties and grain structure. Machining of Ti alloys is to some extent more difficult than that of austenitic stainless steels since they yield under the tool pressure due to

their low Young's modulus. For this same reason the tools used in machining tend to stick to the material. Therefore, sharp tools, rigid setups, heavy feeds, slow speeds, and abundant coolant are required (Breme and Biehl, 1998).

Metallic macroporous structures in orthopedic implants are attracting increasing attention because they combine high strength, which is important to avoid deformation or fracture, relatively low stiffness that reduces the stress-shielding effect, high toughness that prevents brittle fracture, and porosity that allows full bone in-growth and stable long-term fixation. Some fabrication methods used to obtain both open-cell or closed-cell porous metallic structures include sintering of Ti powder, plasma spraying, combustion synthesis, replication, and rapid prototyping (Bansiddhi et al., 2008; Ryan et al., 2008).

## CORROSION RESISTANCE

To some extent, interest in Ti and its alloys for biomaterials applications stems from their superior corrosion resistance when compared to other metals and alloys. This is attributed to the spontaneous formation of a few nm thick titanium dioxide film that protects the metal from further oxidation (Textor et al., 2001). This behavior depends on alloy composition and corrosive medium (Steinemann et al., 1993): anodic polarization tests indicate that Ti-12Mo-6Zr-2Fe protective oxide has a breakdown resistance equal to that of Ti-6Al-4V, whereas for Ti-5Mo-5Zr-3Al alloy, corrosion current densities are lower than for cpTi (Steinemann et al., 1993; Wang et al., 1993). In addition, electrochemical measurements for Ti-13Nb-13Zr also confirmed the potential of Ti, Nb, and Zr to develop highly protective passive layers, resulting in a better corrosion resistance compared to Ti-6Al-4V (Mishra et al., 1993; Cai et al., 2003).

## BIOCOMPATIBILITY AND SURFACE MODIFICATION

The biocompatibility of a metallic alloy has to be understood in terms of both the biocompatibility of the alloy itself, which is closely associated with its corrosion resistance, and the biocompatibility of its by-products as a result of corrosion. It is generally accepted that Ti and its alloys are relatively "biointer," and exhibit acceptable *in vitro* and *in vivo* responses for the desired application. When implanted in bone, tissue heals in close apposition to the metal, although there maybe a thin fibrous layer separating the metallic implant and the bone. In order to improve osteointegration, bioactivity, biocompatibility, and corrosion resistance, several surface treatments based on chemical and physical modifications have been developed (Liu et al., 2004). Methods include chemical and electrochemical treatment, sol-gel, chemical vapor deposition (CVD), and biochemical modification, while physical methods include machining, grinding, polishing, blasting, thermal and plasma spraying, physical vapor deposition, and ion

implantation and deposition, among others. The aim of all these methods is to obtain specific surface topography and chemistry to improve either the mechanical bone/implant interlocking, or the deposition of an apatite or another calcium phosphate bioactive layer to promote direct material–bone bonding, or the activation of particular cell responses by the use of specific biomolecules, such as peptides and proteins (Endo, 1995; Sargeant et al., 2008).

## MECHANICAL PROPERTIES

Ti and its alloys are very attractive for use in different biomedical devices, particularly orthopedics, due to their elastic modulus which is closer to that of bone in comparison to other alloys. The mechanical properties of cpTi and some Ti-based alloys are summarized in Table A.1. The Young's moduli of  $\alpha + \beta$  and  $\beta$ -type titanium alloys for biomedical applications such as Ti-6Al-4V and Ti-35Nb-5Ta-7Zr are much lower than those of stainless steel and Co-based alloys. However, their Young's moduli are still significantly higher than that of cortical bone. Much effort is currently being carried out to develop new alloys with low elastic modulus that mimic that of bone tissue. Some Ti-based alloys within systems such as Ti-Zr, Ti-Mo, Ti-Ta, Ti-Ta-Zr, Ti-Nb-Hf, Ti-Nb-Zr, Ti-Nb-Sn, Ti-Nb-Ta-Zr, Ti-Fe-Ta, Ti-Mo-Zr-Sn, Ti-Sn-Nb-Ta, Ti-Mo-Zr-Fe, Ti-Mo-Nb-Si, Ti-Mo-Ga, Ti-Mo-Ge, and Ti-Mo-Al have recently been reported as potential biomaterials (Niinomi 1999; Nitta et al., 2001). Many of these alloys are  $\beta$ -type, and contain rather large percentages of Nb, Ta, Zr, Mo, and/or Sn, as these elements are relatively non-toxic and non-allergenic, as reported in previous studies (Ahmed et al., 1995; Steinemann 1980).

Among the alloys under investigation, the Ti-Nb-Ta-Zr system known as Gum metal (Ti-29Nb-13Ta-4.6Zr) (Saito, 2001) is gaining attention in the field because of its "super elastic" properties. This alloy has a Young's

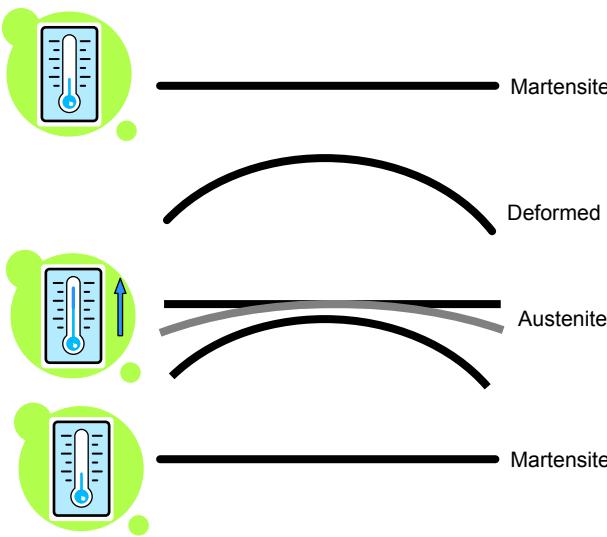
modulus of 40 GPa, and an elastic strain of 2.5% (Niinomi et al., 2002). Another alloy, Ti-35Nb-7Zr-5Ta, also known as TiOsteum®  $\beta$ -Ti alloy, is an alloy that has shown enhanced osseointegration, improved ductility, adequate mechanical strength, optimal hot and cold workability, and low elastic modulus (55 GPa) (Jablokov et al., 2005).

## NiT ALLOY

Nitinol (*Nickel-Titanium Naval Ordnance Laboratory*), an equiatomic alloy of nickel and titanium with shape memory properties, was discovered in the early 1960s by Buehler and his co-workers (Buehler and Wang, 1967). Since then, intensive research has been carried out in order to elucidate the mechanics of its basic behavior. Although NiTi had been proposed and used in different clinical applications, such as clamps for orthopedic and traumatological bone fixation, filters to retain emboli in vascular surgery or orthodontic wires, it was only in the mid-1990s that the first widespread commercial NiTi stents made their appearance. At present, NiTi alloys have been introduced in the medical implant field for their superelastic and shape memory alloy properties, despite related drawbacks associated with Ni ionic release (Huang et al., 2003). Ni is allergenic at high concentrations, and thus the use of Ti-Ni shape memory alloys is quite restrictive (Cederbrant et al., 2003). NiTi shape memory alloy also exhibits two different temperature-dependent crystal structures or phases, named martensite, low temperature phase, and austenite, high temperature or parent phase. When martensite NiTi is heated, it transforms into austenite. The temperature at which this phenomenon starts is called austenite start temperature ( $A_s$ ). The temperature at which this phenomenon is completed is called austenite finish temperature ( $A_f$ ). When austenite NiTi is cooled, it transforms into martensite. The temperature at which this

**TABLE A.1** Titanium Alloys Developed for Orthopedic Applications and Their Mechanical Properties (Adapted from Long and Rack, 1998)

Alloy	Microstructure	Elastic Modulus E (GPa)	Yield Strength YS (MPa)	Ultimate Strength UTS (MPa)
cpTi	$\alpha$	105	692	785
Ti-6Al-4V	$\alpha/\beta$	110	850–900	960–970
Ti-6Al-7Nb	$\alpha/\beta$	105	921	1024
Ti-5Al-2.5Fe	Metastable $\beta$	110	914	1033
Ti-15Mo-5Zr-3Al	Metastable $\beta$	82	771	812
Ti-Zr	Cast $\alpha'/\beta$	N/A	N/A	900
Ti-13Nb-13Zr	$\alpha'/\beta$	79	900	1030
Ti-15Mo-3Nb-0.30	Metastable $\beta$ + silicides	82	1020	1020
Ti-35Nb-5Ta-7Zr	Metastable $\beta$	55	530	590
Ti-35Nb-5Ta-7Zr-0.40	Metastable $\beta$	66	976	1010
Stainless steel 316L	—	205–210	170–750	465–950
Co-Cr-Mo	—	220–230	275–1585	600–1785
Bone	—	10–40		90–140



**FIGURE A.1** Schematic of the shape memory effect created when the surrounding temperature changes; NiTi alloy modifies its shape to a preprogrammed structure due to the austenite-to-martensite phase transformations.

phenomenon starts is called martensite start temperature ( $M_s$ ). The temperature at which martensite is again completely reverted is called martensite finish temperature ( $M_f$ ) (Buehler and Wang, 1967).

$A_s$ ,  $A_f$ ,  $M_s$ , and  $M_f$  depend on the chemical composition of the alloy, and can be adjusted by introducing small variations in the almost equiatomic composition of these alloys. The unique behavior of NiTi is based on the temperature-dependent austenite-to-martensite phase transformations on an atomic scale, which is also called thermoelastic martensitic transformation, and causes the shape recovery as a result of the need for the crystal lattice structure to accommodate to the minimum energy state for a given temperature (Otsuka and Wayman, 1998). As a consequence, the shape memory effect is created when the surrounding temperature changes; NiTi alloy modifies its shape to a preprogrammed structure (see Figure A.1).

Superelasticity (or pseudoelasticity) refers to the ability of NiTi to return to its original shape upon unloading after substantial deformation. This is based on stress-induced martensite formation. The application of an external stress causes macroscopic deformation which is accommodated by the formation of martensite at temperatures higher than  $M_s$ . When the stress is released, the martensite transforms back into austenite, and the specimen returns back to its original shape. Superelastic NiTi can be strained several times, i.e., cycled, without being plastically deformed, reflecting a rubber-like behavior. While most metals sustain plastic deformation by slip or dislocation movement, NiTi sustains large elastic deformations by simply changing the orientation of its crystal structure through the movement of twin boundaries. This phenomenon is only observed over a specific range of temperatures. The highest temperature at which

**TABLE A.2** | Mechanical Properties of NiTi Alloy (Duerig and Pelton, 1994)

	NiTi	
	Austenitic	Martensitic
Ultimate tensile strength (MPa)	800–1500	103–1100
Tensile yield strength (MPa)	100–800	50–300
Modulus of elasticity (GPa)	70–110	21–69
Elongation at failure (%)	1–20	up to 60

martensite can no longer be stress induced is called  $M_d$ . Above  $M_d$ , NiTi alloy deforms in the austenite phase by slipping, like ordinary metals. Below  $A_s$ , the material is martensitic and does not recover. Superelasticity appears in a temperature range around  $A_f$  up to  $M_d$ . The ability to recover is maximal when temperature is close to  $A_f$  (Duerig and Pelton, 1994).

The mechanical properties of NiTi depend on the phase which is present at a certain temperature (Buehler and Wang, 1967; Van Humbeeck et al., 1998). Fully austenitic NiTi material generally has suitable properties for surgical implantation. The common mechanical properties of martensitic and austenitic NiTi are presented in Table A.2 (Buehler and Wang, 1967; Honma, 1987; Breme and Biehl, 1998; Van Humbeeck et al., 1998).

NiTi has unique high fatigue and ductile properties, which are also related to its martensitic transformation. These properties are favorable for their use in orthopedic implants. However, wear resistance has been reported to be lower when compared to the Co–Cr–Mo alloys (Sekiguchi, 1987). Moreover, NiTi is a non-magnetic alloy and consequently, magnetic resonance imaging is possible.

## SURFACE MODIFICATIONS OF NiTi

It is well known that titanium is well tolerated when implanted in the human body; however, it is also known that certain nickel levels are toxic and may trigger allergic responses. NiTi alloys form a passive titanium oxide layer that improves the metal resistance to corrosion, and acts as a barrier to Ni oxidation and release. The original NiTi surface has shown a tendency towards preferential oxidation of titanium. This behavior is in agreement with the fact that free enthalpy formation of titanium oxides is negative, and exceeds in absolute value the enthalpy formation of nickel oxides by at least two to three times (Chan et al., 1990). As a result, Ni is mostly present in an ionic state on the NiTi surfaces. Various approaches are currently under development to prevent undesirable Ni release and improve NiTi tolerance in the body. Laser and plasma treatment, ion implantation, hydroxyapatite, as well as TiN and TiCN chemical vapor deposits, have been used to modify the surface of NiTi alloys (Averbach and Kirk, 1985; Filip et al., 1997; Villermaux et al., 1997). Induction or development of bioactive surfaces

by immersion of the material in either simulated body fluid (SBF) or Hank's solution, and protein coatings are also strategies for improving NiTi biocompatibility and reducing Ni release. In addition, techniques such as oxidation in air/oxygen atmosphere, oxidation in boiling water and steam, and chemical/electrochemical passivation have been successfully used (Michiardi et al., 2005).

## APPLICATIONS

Superelasticity is a unique property of great interest in the biomedical field, and this is the reason why NiTi alloy has been proposed for different applications, such as orthopedic plates, screws and staples; cardiovascular devices, mainly stents; surgical instruments, such as surgical endoscopic tools and orthodontic devices (Duerig et al., 1999).

Since superelasticity and shape memory effect are highly advantageous, but the risk of metallic allergy is still high, investigations in developing Ni-free superelastic and shape memory titanium alloys containing non-toxic elements are of significant interest to researchers in the field. Some candidates that are currently investigated include the Ti–Nb–Sn system alloy. The martensite transformation temperature ( $M_s$ ) of this system decreases by increasing the amount of Nb or Sn, and the shape memory effect is recognized when the alloy is deformed below austenite transformation temperature ( $A_f$ ) similar to the case of Ti–Ni. It has been reported that superelastic strain of 3.5% is obtained at the composition of Ti-18Nb-4Sn (Nitta et al., 2001). Other systems being investigated also include Ti–Mo–Ga, Ti–Mo–Ge or Ti–Mo–Al, Ti–Ta, Ti–Ta–Zr, and Ti–Sc–Mo (Niinomi, 2003).

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## B. STAINLESS STEELS

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### INTRODUCTION

There are a large number of stainless steels available commercially but only a few of these alloys are used as biomaterials for implantable devices. Use of stainless steel implants began in the 1920s and 1930s; stainless steel applications have expanded as new medical procedures and improved materials were developed.

The performance of these alloys depends on their chemical composition and processing history. While 316L is the most common stainless steel, alloys with enhanced corrosion resistance and mechanical properties are available.

### METALLURGICAL AND CHEMICAL CONSIDERATIONS

Implantable stainless steels all have a crystal structure known as face centered cubic (models of metallic crystal structures are shown in Figure I.3.1.1, Chapter I.1.3); in steels this crystal structure is called austenite. Austenitic stainless steels are essentially non-magnetic; this is crucial since patients may be exposed to high intensity magnetic fields during MRI examinations. It should be noted that modest amounts of heating and displacement can occur for these alloys under MRI exposure. Under some processing conditions, it is possible to form different phases within the austenitic alloys such as delta ferrite (which is magnetic); the presence of these additional phases is deleterious and is not allowed under the standard specifications that control these materials for implant use.

**Table B.1** shows the chemical composition ranges specified for several common implantable stainless steels. Chromium is present in these alloys, primarily to form a protective  $\text{Cr}_2\text{O}_3$  surface layer (passive film) that is crucial to their corrosion resistance. Since chromium stabilizes the magnetic ferrite (body centered cubic) structure, other alloying elements must be added to stabilize the desired austenite phase. This role is filled primarily by additions of nickel, manganese, and nitrogen. Nitrogen additions also increase mechanical strength and corrosion resistance. Molybdenum additions have a beneficial impact on the pitting corrosion resistance of stainless steels.

Carbon is controlled to be at low levels to prevent the formation of chromium carbides (the “L” in 316L designates low carbon). Formation of these carbides can result in a phenomenon known as sensitization. If enough carbon is available, chromium carbides can form when austenitic stainless steels are held at temperatures in the range of 450°C to 815°C; the time required to form these carbides depends on the temperature. Under these conditions, carbides tend to form preferentially along grain boundaries, leaving the adjacent areas with depleted chromium levels which are prone to attack by corrosion. Slow cooling after welding is a classic process that can cause sensitization if time and cooling rates are not controlled.

Examination of the chemical compositions in **Table B.1** reveals some trends that have changed over time in the chemical composition of implantable stainless steels. While 316 and 316L stainless steels have been used successfully for implants for more than 50 years, stronger and more corrosion-resistant alloys have been developed. The alloys known as Rex 734 (also known as Ortron 90) and 22-13-5 were developed in the 1980s. These alloys contain higher levels of chromium, manganese,

**TABLE B.1 Compositions of Common Implantable Stainless Steels (Weight Percent)**

Alloy	Cr	Ni	Mn	Mo	C	N	Nb	V	Si	Cu	P	S
316L ASTM F138, ISO 5832-1	17–19	13–15	<2 max	2.25–3	<0.030	<0.10	–	–	<0.75	<0.5	<0.025	<0.010
22-13-5 ASTM F1314	20.5–23.5	11.5–13.5	4–6	2–3	<0.030	0.2–0.4	0.1–0.3	0.1–0.3	<0.75	<0.5	<0.025	<0.010
Rex 734, Ortron 90 ASTM F1586 ISO 5832-9	19.5–22	9–11	2–4.25	2–3	<0.08	0.25–0.5	0.25–0.8	–	<0.75	<0.25	<0.25	<0.010
BioDur® 108 ASTM F 2229	19–23	<0.050	21–24	0.5–1.5	<0.08	0.85–1.10	–	–	<0.75	<0.25	<0.03	<0.010

and nitrogen than 316L, leading to improved mechanical properties and corrosion resistance. Recent concern about patients with an allergic response to nickel (see Orthopedic Applications, Chapter II.5.6 for additional discussion of this topic) has led to development of stainless steels which are essentially nickel free. One example is an alloy known as BioDur®108, which uses additions of manganese and nitrogen instead of nickel to stabilize the austenite phase. The nitrogen level in this alloy (1%) is much higher than the level found in the prior implantable stainless steels.

Empirical formulas have been developed to describe the contribution of alloying elements to pitting corrosion resistance of austenitic stainless steels; this is known as the Pitting Resistance Equivalent number or PRE. The formula for PRE depends on several factors, including the amount of nitrogen in the alloy. At low nitrogen levels an appropriate approximation of the PRE is:  $\text{PRE} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$ ; at nitrogen levels nearing 1% a more appropriate approximation is:  $\text{PRE} = \% \text{Cr} + 3.2 \times \% \text{Mo} + 8 \times \% \text{N}$  (Gebeau and Brown, 2001). Higher PRE numbers indicate improved resistance to pitting corrosion.

## MECHANICAL PROPERTIES

The mechanical properties of metals and alloys depend on their chemical composition and processing history. To understand how these factors influence mechanical properties it is important to consider the mechanisms involved when permanent deformation takes place (plastic deformation). Plastic deformation occurs primarily by movement of dislocations within the material (“slip”). Dislocations are defects or disturbed regions in the crystal lattice. If the resistance to dislocation motion is increased, strength properties such as yield strength increase, while deformation capacity (ductility) decreases.

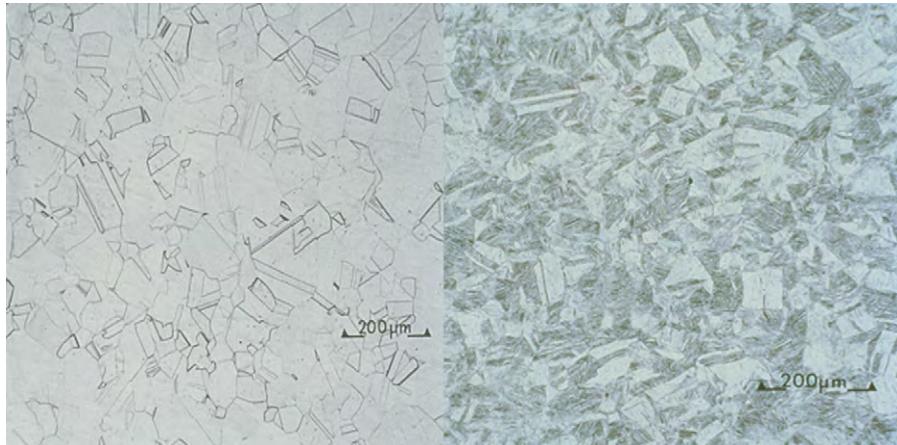
Chemical composition also influences strength by a process known as solid solution strengthening. In stainless steels the metallic alloying elements (Cr, Ni, etc.) replace iron atoms at random locations within the crystal structure. Since the various atoms are not the same

size, additions of alloying elements lead to distortion of the crystal lattice. This distortion makes deformation of the material more difficult (dislocation movements), thus increasing strength (and generally decreasing ductility). Smaller atoms, such as N, fit within the gaps between the larger metallic atoms; for this reason they are often referred to as interstitials. Additions of these atoms lead to large strength increases due to the interactions between the solute atom and dislocations.

Another strengthening mechanism available for these materials involves work hardening (also known as “cold-working”). Processes commonly used to change the mechanical properties of other alloys such as aging reactions during heat treatment are not applicable to austenitic stainless steels.

Work hardening occurs due to the increased difficulty of dislocation motion, as more and more dislocations interact within the material. As the material is deformed, increasing quantities of dislocations develop within the grains of the alloy. If the deformation process takes place at high temperatures (which is typical of the large-scale processes used to produce metal products), or if the material is heated above its recrystallization temperature after deformation, the dislocations are removed by formation of new, annealed grains (recrystallization). Deformation at lower temperatures does not eliminate dislocations. As the density of dislocations within the material increases, they begin to interact making further dislocation motion more difficult. This leads to increases in strength and reductions in ductility. More information on solid solution strengthening and work hardening can be found in a number of materials science textbooks (Hosford, 2005; Meyers & Chawla, 2008).

Evidence of deformation within the grains of a moderately cold-worked 316L sample is shown in Figure B.1, which compares the structure of annealed and ~30% cold-worked 316L. The amount of cold-work is routinely specified by the percentage reduction of area; this is calculated by  $(A_i - A_f / A_i) \times 100$ , where  $A_i$  is the initial cross-sectional area of the product and  $A_f$  is the final cross-sectional area. As the amount of cold-work



**FIGURE B.1** Microstructures of annealed 316L (left), and ~30% cold-worked 316L (right). Deformation within many of the grains of the cold-worked material is evident.

**TABLE B.2 Approximate Mechanical Properties of Stainless Steels**

Alloy	Material Condition	Ultimate Tensile Strength (MPa)	Yield Strength (MPa)	%Elongation	$10^7$ Cycle Endurance Limit (MPa)	Reference
316L	Annealed	550	240	55	180	Shetty & Ottersberg, 1995
316L	30% Cold-worked	896	827	20	380	Shetty & Ottersberg, 1995
316L	60% Cold-worked	1240	1000	12	450	Shetty & Ottersberg, 1995
Rex 734	Hot forged	1140–1230	1050–1179	15–19	585	Windler & Steger, 2003
22-13-5	Annealed	965	760	35	380	Shetty & Ottersberg, 1995
22-13-5	30% Cold-worked	1240	1170	15	530	Shetty & Ottersberg, 1995
22-13-5	60% Cold-worked	1585	1480	9	670	Shetty & Ottersberg, 1995
BioDur®108	Annealed	827–930	517–605	30–50	380	ASTM F 2229 and Technical Data Sheet BioDur®108
BioDur®108	35% Cold-worked	1580	1350	15		Technical Data Sheet BioDur®108
BioDur®108	65% Cold-worked	2000	1790	5		Technical Data Sheet BioDur®108

increases, strength parameters (yield strength and ultimate strength) increase (along with hardness), while the ductility decreases. This behavior gives designers the ability to specify a wide range of mechanical properties by proper selection of the alloy composition, processing temperature, and the amount of cold-work. Table B.2 lists approximate tensile and fatigue strength properties for some implantable stainless steels produced under different conditions. The influence of chemical composition and amount of cold-work on mechanical properties is evident in these data.

It should be noted that there are limits to the uniformity of the cold-working response which is a function of the cross-sectional area of the material. In practical terms, this means that a large cross-section may have a gradient in the amount of cold-work; thus the outer regions of the material may be more heavily worked than the interior. Another effect of cold-working is that heavily worked stainless steels, such as 304 and 305, can become magnetic due to a

stress-induced transformation of crystal structure from austenite (non-magnetic) to martensite (magnetic). This can result in negative clinical results if fragments of these alloys, which are routinely used as guide wires, break off during a procedure (FDA Public Health Notification, 2008). It is also important to realize that elevated temperature processes such as welding will result in softening of a cold-worked material, and reduction of mechanical properties to annealed levels.

A high level of fatigue strength is necessary for many stainless steel medical devices (see Chapter I.1.3 of this volume for more information on fatigue). The fatigue properties of metallic materials depend on a number of factors including: composition; grain size; processing history; surface finish; and test method. The fatigue data shown in Table B.2 provide approximate values; these data should not be used for implant design purposes since the properties of specific devices are strongly influenced by manufacturing processes, product design features, the inherent variation from batch to batch of raw

material, and variability in the processes used to produce the device.

## CORROSION BEHAVIOR

With the exception of noble metals such as gold or platinum, the common implantable metals and alloys rely on the formation of protective oxide films to control corrosion of the material to acceptable levels. These oxides are commonly referred to as passive films. They are very thin (typically less than 100 microns), dense, and adhere strongly to the underlying substrate. They limit transport of metallic ions to the implant surface. The alloys that contain substantial amounts of chromium (austenitic stainless steels and implantable cobalt base alloys) form a Cr<sub>2</sub>O<sub>3</sub> layer while alloys rich in titanium (titanium alloys and Nitinol) form a TiO<sub>2</sub> layer. More detailed information on passive layers is presented in Chapter II.5.6 Orthopedic Applications. Chapter II.4.4 Degradative Effects of the Biological Environment on Metals and Ceramics includes a great deal of information on corrosion of implant metals.

In general terms, the austenitic stainless steels are not considered to be quite as corrosion resistant as either cobalt-chromium alloys or titanium alloys. The more recent alloys (22-13-5, Rex 734, and BioDur®108) exhibit improved corrosion resistance when compared to 316L, due to their higher levels of Cr and N. One measure of relative corrosion resistance is the pitting potential, as determined in an anodic polarization test; pitting potential varies somewhat depending on the testing conditions, but one author found it was 346 mV for 316L, 1030 mV for 22-13-5, and 1120 mV for BioDur®108 (Zardiackas et al., 2003). Another factor which influences the corrosion of stainless steels is the presence of foreign particles, known as inclusions. These are typically oxide particles such as alumina or silicates which are formed during the initial melting of the alloy and become trapped within the material during subsequent processing. Since these inclusions have different corrosion behavior than the alloy, they can act as corrosion initiation sites if they are found at the surface of a component. Careful control of alloy melting practice and subsequent processing is required to minimize the number of inclusions within these alloys. The ASTM specifications for implantable stainless steels include sections that limit the number and size of inclusions.

## SUMMARY

A limited group of austenitic stainless steels are routinely implanted because they offer sufficient corrosion resistance and mechanical strength for long-term applications in the human body. Although 316L is one of the oldest and most common alloys in use, more recent developments have led to stainless steels with improved mechanical strength and corrosion resistance. The corrosion resistance and mechanical properties of these materials are determined by chemical composition, and the processing used to produce the component.

The ability to choose from a range of properties is advantageous. A soft, ductile, annealed condition can be specified for a component that must be contoured in the operating room, while a higher strength, less ductile, work-hardened material may be used for devices that must withstand higher fatigue loads. A long history of success in an application may also be a factor in the use of stainless steels in some devices.

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