**Stainless Steels:`**

The first stainless steel utilized for implant fabrication was the 18-8 (type 302), which is stronger and more resistant to corrosion than the vanadium steel. Vanadium steel is no longer used in implants since its corrosion resistance is inadequate *in vivo*. Later 18-8sMo stainless steel was introduced which contains a small percentage of molybdenum to improve the corrosion resistance in chloride solution (salt water). This alloy became known as *type 316 stainless steel*. In the 1950s the carbon content of 316 stainless steel was reduced from 0.08 to a maximum amount of 0.03% for better corrosion resistance to chloride solution and to minimize the sensitization, and hence became known as type *316L stainless steel*. The minimum effective concentration of chromium is 11% to impart corrosion resistance in stainless steels. The chromium is a reactive element, but it and its alloys can be *passivated* by 30% nitric acid to give excellent corrosion resistance.

Types 316 and 316L, are most widely used for implant fabrication. These cannot be hardened by heat treatment but can be hardened by cold-working. This group of stainless steels is nonmagnetic and possesses better corrosion resistance than any others. The inclusion of molybdenum enhances resistance to *pitting corrosion* in salt water. The American Society for Testing and Materials (ASTM) recommends type 316L rather than 316 for implant fabrication. The specifications for 316L stainless steel are given in Table 1.1.

**TABLE 1.1** Compositions of 316L Stainless Steel [American Society for Testing and Materials ASTM]

|  |  |
| --- | --- |
| Element | Composition (%) |
| Carbon  Manganese  Phosphorus  Sulfur  Silicon  Chromium  Nickel  Molybdenum | 0.03 max  2.00 max  0.03 max  0.03 max  0.75 max  17.00–20.00  12.00–14.00  2.00–4.00 |

The nickel stabilizes the austenitic phase [γ, face centered cubic crystal (fcc) structure] at room temperature and enhances corrosion resistance. The minimum amount of Ni for maintaining austenitic phase is approximately 10%. Table 1.2 gives the mechanical properties of 316L stainless steel. A wide range of properties exists depending on the heat treatment (annealing to obtain softer materials) or cold working (for greater strength and hardness).



The engineer must consequently be careful when selecting materials of this type.

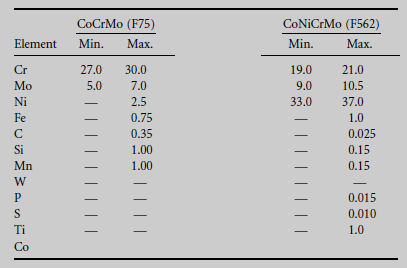
Even the 316L stainless steels may corrode inside the body under certain circumstances in a highly stressed and oxygen depleted region, such as the contacts under the screws of the bone fracture plate. Thus, these stainless steels are suitable for use only in temporary implant devices such as fracture plates, screws, and hip nails. Surface modification methods such as anodization, passivation, and glow-discharge nitrogen implantation are widely used in order to improve corrosion resistance, wear resistance, and fatigue strength of 316L stainless steel.

**CoCr Alloys:**

There are two types of cobalt-chromium alloys: (1) the castable CoCrMo alloy and (2) the CoNiCrMo alloy, which is usually wrought by (hot) forging. The castable CoCrMo alloy has been used for many decades in dentistry and, relatively recently, in making artificial joints. The wrought CoNiCrMo alloy is relatively new, now used for making the stems of prostheses for heavily loaded joints such as the knee and hip. Table 1.3 shows, the compositions are quite different from each other.

**TABLE 1.3** Chemical Compositions of CoCr Alloys [American Society for Testing and

Materials, F75–87, p.42; F562–84, p.150, 1992]



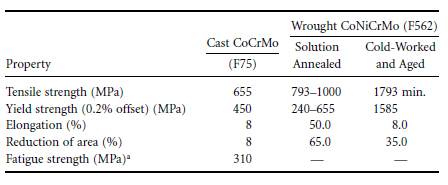
The two basic elements of the CoCr alloys form a solid solution of up to 65% Co. The molybdenum is added to produce finer grains which results in higher strengths after casting or forging. The chromium enhances corrosion resistance as well as solid solution strengthening of the alloy.

The CoNiCrMo alloy is highly corrosion resistant to seawater (containing chloride ions) under stress. Cold working can increase the strength of the alloy. However, there is a considerable difficulty of cold working on this alloy, especially when making large devices such as hip joint stems. Only hot-forging can be used to fabricate a large implant with the alloy.

The abrasive wear properties of the wrought CoNiCrMo alloy are similar to the cast CoCrMo alloy (about 0.14 mm/yr in joint simulation tests with ultra-high molecular weight polyethylene acetabular cup); however, the former is not recommended for the bearing surfaces of joint prostheses because of its poor frictional properties with itself or other materials. The superior fatigue and ultimate tensile strength of the wrought CoNiCrMo alloy make it suitable for the applications, which require long service life without fracture or stress fatigue. Such is the case for the stems of the hip joint prostheses.

The mechanical properties required for CoCr alloys are given in Table 1.4. As with the other alloys, the increased strength is accompanied by decreased ductility. Both the cast and wrought alloys have excellent corrosion resistance.

TABLE 1.4 Mechanical Property Requirements of CoCr Alloys (ASTM).



Experimental determination of the rate of nickel release from the CoNiCrMo alloy and 316L stainless steel in 37°C showed an interesting result. Although the cobalt alloy has more initial release of nickel ions into the solution, the rate of release was about the same (3×10–10 g/cm2/day) for both alloys. This is rather surprising since the nickel content of the CoNiCrMo alloy is about three times that of 316L stainless steel.

The metallic products released from the prosthesis because of wear, corrosion, and fretting may impair organs and local tissues. In vitro studies have indicated that, particulate Co is toxic to human osteoblast like cell lines and inhibits synthesis of type-I collagen, osteocalcin, and alkaline phosphatase in the culture medium. However, particulate Cr and CoCr alloys are well tolerated by cell lines with no significant toxicity. The toxicity of metal extracts in vitro have indicated that Co and Ni extracts at 50% concentration appear to be highly toxic since all viability parameters were altered after 24 h. However, Cr extract seems to be less toxic than Ni and Co.

The modulus of elasticity for the CoCr alloys does not change with the changes in their ultimate tensile strength. The values range from 220 to 234 GPa, which are higher than other materials such as stainless steels. This may have some implications of different load transfer modes to the bone in artificial joint replacements. Low wear (average linear wear was 4.2 μm/yr) has been recognized as an advantage of metal on-metal hip articulations because of its hardness and toughness.

**Ti Alloys:**

Attempts to use titanium for implant fabrication dates to the late 1930s. It was found that, titanium was tolerated in cat femurs, as was stainless steel and Vitallium® (CoCrMo alloy). Titanium’s lightness (4.5 g/cm3 see Table 1.5) and good mechanochemical properties are salient features for implant application.

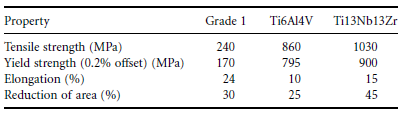


The impurity contents separate them; oxygen, iron, and nitrogen should be controlled carefully. Oxygen in particular has a great influence on the ductility and strength.

One titanium alloy (Ti6Al4V) is widely used to manufacture implants and its mechanical requirements are given in Table 1.6. The main alloying elements of the alloy are aluminum (5.5~6.5%) and vanadium (3.5~4.5%). The Ti6Al4V alloy has approximately the same fatigue strength (550 MPa) of CoCr alloy after rotary bending fatigue tests.

**TABLE 1.6** Mechanical Properties of Ti and Its Alloys (ASTM F136) .





Titanium is an allotropic material, which exists as a hexagonal close packed structure (hcp,α -Ti) up to 882°C and body-centered cubic structure (bcc,β-Ti) above that temperature. Titanium alloys can be strengthened and mechanical properties varied by controlled composition and thermomechanical processing techniques. The addition of alloying elements to titanium enables it to have a wide range of properties: (1) Aluminum tends to stabilize the α -phase, that is increase the transformation temperature from α – to β -phase. (2) vanadium stabilizes the β -phase by lowering the temperature of the transformation from α to β.

Titanium derives its resistance to corrosion by the formation of a solid oxide layer to a depth of 10 nm. Under in vivo conditions, the oxide (TiO2) is the only stable reaction product. However, micromotion at the cement–prosthesis and cement–bone are inevitable; consequently, titanium oxide and titanium alloy particles are released in cemented joint prostheses. Sometimes this wear debris accumulates as periprosthetic fluid collects and triggers giant cell response around the implants. This cystic collection continues to enlarge and aspiration reveals “dark” heavily stained fluid containing titanium wear particles and histiocytic cells. Histological examination of the stained soft tissue showed “fibrin necrotic debris” and collagenous, fibrous tissue containing a histiocytic and foreign body giant cell infiltrate. The metallosis, black staining of the periprosthetic tissues, has been implicated in knee implants.

The titanium implant surface consists of a thin oxide layer and the biological fluid of water molecules, dissolved ions, and biomolecules (proteins with surrounding water shell) as shown in Fig. 1.7. The microarchitecture (microgeometry, roughness, etc.) of the surface and its chemical compositions are important due to the following reasons:

1. Physical nature of the surface either at the atomic, molecular, or higher level relative to the dimensions of the biological units may cause different contact areas with biomolecules, cells, etc. The different contact areas, in turn, may produce different perturbations and types of bonding of the biological units, which may influence their conformation and function.

2. Chemical composition of the surface may produce different types of bonding to the biomolecules, which may then also affect their properties and function. Metals undergo chemical reactions at the surface depending on the environment which cause the difficulties of understanding the exact nature of the interactions.

The surface–tissue interaction is dynamic rather than static, i.e., it will develop into new stages as time passes, especially during the initial period after implantation. During the initial few seconds after implantation, there will be only water, dissolved ions, and free biomolecules in the closest proximity of the surface but no cells. The composition of biofluid will then change continuously as inflammatory and healing processes proceed, which in turn also probably causes changes in the composition of the adsorbed layer of biomolecules on the implant surface until quasi-equilibrium sets in. Eventually, cells and tissues will approach the surface and, depending on the nature of the adsorbed layer, they will respond in specific ways that may further modify the adsorbed biomolecules. The type of cells closest to the surface and their activities will change with time. For example, depending on the type of initial interaction, the final results may be fibrous capsule formation or tissue integration.



**FIGURE 1.7** (a) Interface between a titanium implant and bioliquid and (b) the cell surface interaction.

Osseointegration is defined as direct contact without intervening soft tissue between viable remodeled bone and an implant. Surface roughness of titanium alloys have a significant effect on the bone apposition to the implant and on the bone implant interfacial pull out strength. The average roughness increased from 0.5 to 5.9 μm and the interfacial shear strength increased from 0.48 to 3.5 MPa. Highest levels of osteoblast cell attachment are obtained with rough sand blast surfaces where cells differentiated more than those on the smooth surfaces. Chemical changes of the titanium surface following heat treatment are thought to form a TiO2 hydrogel layer on top of the TiO2 layer, as shown in Fig. 1.8. The TiO2 hydrogel layer may induce the apatite crystal formation.

In general, on the rougher surfaces there are lower cell numbers, decreased rate of cellular proliferation, and increased matrix production compared to smooth surfaces. Bone formation appears to be strongly related to the presence of transforming growth factor β1 in the bone matrix.



**FIGURE 1.8** Chemical change of titanium implant surface of alkali following heat treatment.

**TiNi Alloys:**

The *titanium–nickel* alloys show unusual properties i.e., after it is deformed the material can snap back to its previous shape following heating of the material. This phenomenon is called *shape memory effect* (SME). The equiatomic TiNi or NiTi alloy (Nitinol) exhibits an exceptional SME near room temperature: if it is plastically deformed below the transformation temperature, it revertsback to its original shape as the temperature is raised. The SME can be generally related to a diffusionless martensitic phase transformation which is also thermoelastic in nature, the thermoelasticity being attributed to the ordering in the parent and martensitic phases.

Another unusual property is the superelasticity, which is shown schematically in Fig. 1.9. As can be seen, the stress does not increase with increased strain after the initial elastic stress region and upon release of the stress or strain the metal springs back to its original shape in contrast to other metals such as stainless steel. The superlastic property is utilized in orthodontic archwires since the conventional stainless steel wires are too stiff and harsh for the tooth. In addition, the shape memory effect can also be utilized.

Some possible applications of shape memory alloys are orthodontic dental archwire, intracranial aneurysm clip, *vena cava* filter, contractile artificial muscles for an artificial heart, vascular stent, catheter guide wire, and orthopedic staple. There is no significant difference between titanium and NiTi in the inhibition of mitosis in human fibroblasts. NiTi showed lower percentage bone and bone contact area than titanium and the Ti6Al4V alloy.

 The mechanical properties of NiTi alloys are especially sensitive to the stoichiometry of composition (typical composition is given in Table 1.8) and the individual thermal and mechanical history. Although much is known about the processing, mechanical behavior, and properties relating to the shape memory effect, considerably less is known about the thermomechanical and physical metallurgy of the alloy.

**Dental Metals:**

Dental amalgam is an alloy made of liquid mercury and other solid metal particulate alloys made of silver, tin, copper, etc. The solid alloy is mixed with (liquid) mercury in a mechanical vibrating mixer and the resulting material is packed into the prepared cavity. One of the solid alloys is composed of at least 65% silver and not more than 29% tin, 6% copper, 2% zinc, and 3% mercury. The reaction during setting is thought to

γ+ Hg→ γ+γ1+γ2……………….(1.1)

in which the γ phase is Ag3Sn, the γ1 phase is Ag2 Hg3, and the γ2phase is Sn7Hg. The phase diagram for the Ag-Sn-Hg system shows that over a wide compositional range all three phases are present. The final composition of dental amalgams typically contain 45 to 55% mercury, 35 to 45% silver, and about 15% tin after fully set in about one day.

Gold and gold alloys are useful metals in dentistry as a result of their durability, stability, and corrosion resistance. Gold fillings are introduced by two methods: casting and malleting. Cast restorations are made by taking a wax impression of the prepared cavity, making a mold from this impression in a material such as gypsum silica, which tolerates high temperature, and casting molten gold in the mold. The patient is given a temporary filling for the intervening time. Gold alloys are used for cast restorations, since they have mechanical properties which are superior to those of pure gold.

Corrosion resistance is retained in these alloys provided they contain 75% or more of gold and other noble metals. Copper alloyed with gold significantly increases its strength. Platinum also improves the strength, but no more than about 4% can be added, or the melting point of the alloy is elevated excessively. Silver compensates for the color of copper. A small amount of zinc may be added to lower

the melting point and to scavenge oxides formed during melting. Gold alloys of different composition are available. Softer alloys containing more than 83% gold are used for inlays which are not subjected to much stress. Harder alloys containing less gold are chosen for crowns and cusps which are more heavily stressed.

Malleted restorations are built up in the cavity from layers of pure gold foil. The foils are welded together by pressure at ambient temperature. In this type of welding, the metal layers are joined by thermal diffusion of atoms from one layer to the other. Since intimate contact is required in this procedure, it is particularly important to avoid contamination. The pure gold is relatively soft, so this type of restoration is limited to areas not subjected to much stress.

**Other Metals:**

Several other metals have been used for a variety of specialized implant applications. Tantalum has been subjected to animal implant studies and has been shown very biocompatible. Due to its poor mechanical properties (Table 1.9) and its high density (16.6 g/cm3) it is restricted to few applications such as wire sutures for plastic and neurosurgery and as a radioisotope for bladder tumors. Platinum group metals (PGM) such as Pt, Pd, Rh, Ir, Ru, and Os are extremely corrosion resistant but have poor mechanical properties. They are mainly used as alloys for electrodes such as pacemaker tips because of their high resistance to corrosion and low threshold potentials for electrical conductivity.

Thermoseeds made of 70% Ni and 30% Cu have been produced which possess Curie points in the therapeutic hyperthermia range, approximately 40 to 50°C. Upon the application of an alternating magnetic field, eddy currents are induced, which will provide a continuous heat source through resistive heating of the material. As the temperature of a ferromagnetic substance nears its curie point, however, there is a loss of ferromagnetic properties and a resulting loss of heat output. Thus, selfregulation of temperature is achieved and can be used to deliver a constant hyperthermic temperature extracorporeally at any time and duration.

Surface modifications of metal alloys such as coatings by plasma spray, physical or chemical vapor deposition, ion implantaion, and fluidized bed deposition have been used in industry. Coating implants with tissue compatible materials such as hydroxyapatite, oxide ceramics, Bioglass®, and pyrolytic carbon are typical applications in implants. Such efforts have been largely ineffective if the implants are permanent and particularly if the implants are subjected to a large loading. The main problem is the delamination of the coating or eventual wear of the coating. The added cost of coating or ion implanting hinders the use of such techniques unless the technique shows unequivocal superiority compared to the non-treated implants.

