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doi:10.1186/2052-1847-5-10
Cite this article as: Inui *et al.*: Influence of navigation system updates on total knee arthroplasty. *BMC Sports Science, Medicine, and Rehabilitation* 2013 **5**:10.

Research and development of metals for medical devices based on clinical needs

IOP PUBLISHING SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS

Sci. Technol. Adv. Mater. **13** (2012) 064102 (15pp) doi:10.1088/1468-6996/13/6/064102

TOPICAL REVIEW

Research and development of metals for medical devices based on clinical needs

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Received 4 August 2012
Accepted for publication 18 October 2012
Published 13 December 2012
Online at stacks.iop.org/STAM/13/064102

Abstract

The current research and development of metallic materials used for medicine and dentistry is reviewed. First, the general properties required of metals used in medical devices are summarized, followed by the needs for the development of $\alpha + \beta$ type Ti alloys with large elongation and β type Ti alloys with a low Young's modulus. In addition, nickel-free Ni–Ti alloys and austenitic stainless steels are described. As new topics, we review metals that are bioabsorbable and compatible with magnetic resonance imaging. Surface treatment and modification techniques to improve biofunctions and biocompatibility are categorized, and the related problems are presented at the end of this review. The metal surface may be biofunctionalized by various techniques, such as dry and wet processes. These techniques make it possible to apply metals to scaffolds in tissue engineering.

Keywords: metal, alloy, biomaterial, implant, medical device, biofunction, biocompatibility

1. Introduction

The use of metals has a long history, integral to materials science and engineering. However, metals are sometimes thought as 'unfavorable materials' for medical purposes due to the environmental and health concerns over heavy metals. With the emphasis on safety of metals for medical use, considerable effort is given to the improvement of corrosion resistance and mechanical durability. On the other hand, the technological evolution of ceramics and polymers during the last three decades has made it possible to apply these materials to medical devices; as a result, many metal devices have been replaced with those made of ceramics and polymers. In spite of this development, over 80% of implant devices are made of metals because of their strength, toughness and durability. The advantages of metals in medical devices are the following:

(a) high strength,
(b) high elasticity,
(c) high fracture toughness,
(d) a combination of high elasticity and stiffness and
(e) high electrical conductivity.

When considering the above properties, metals are generally superior to ceramics and polymers for medical devices. Therefore, it is difficult to replace metals in medical devices with ceramics or polymers.

Research and development of metals continue with the purpose of improving mechanical and surface properties, which govern their mechanical and tissue compatibility. In this paper, we review developments in the research on metallic materials used for medicine, including dentistry.

2. General properties required of metals used in medical devices

Metals are essential for orthopedic implants, bone fixators, artificial joints and external fixators since they substitute for the functions of hard tissues in orthopedics. Stents and stent grafts are placed in blood vessels for dilatation. Therefore, elasticity or plasticity for expansion and rigidity for maintaining dilatation are required in the devices. In dentistry, metals are used for restorations, orthodontic wire and dental implants.

The most important property of these biomaterials is safety. Metals implanted in tissues do not show any toxicity

Table 1. Requirements of metals for medical devices.

Required property	Target medical devices	Effect
Elongation to fracture	Spinal fixation; maxillofacial plate	Improvement of durability
Elastic modulus	Bone fixation; spinal fixation	Prevention of bone absorption by stress shielding
Superelasticity Shape memory effect	Multi-purpose	Improvement of mechanical compatibility
Wear resistance	Artificial joint	Prevention of generation of wear debris; improvement of durability
Bioderadability	Stent; artificial bone; bone fixation	Elimination of materials after healing; no need of retrieval
Bone formation Bone bonding	Stem and cup of artificial hip joint; dental implant	Fixation of devices in bone
Prevention of bone formation	Bone screw; bone nail	Prevention of assimilation
Adhesion of soft tissue	Dental implant; trans skin device; external fixation; pacemaker housing	Fixation in soft tissue; prevention of inflectional disease
Inhibition of platelet adhesion	Devices contacting blood	Prevention of thrombus
Inhibition of biofilm formation	All implant devices; treatment tools and apparatus	Prevention of infectious disease
Low magnetic susceptibility	All implant devices; treatment tools and apparatus	No artifact in MRI

without metal ion dissolution by corrosion and/or generation of debris by wear. Therefore, corrosion-resistant materials, such as stainless steel, the Co–Cr–Mo alloy, commercially pure Ti and Ti alloys, are employed. Noble-metal-based alloys, such as Au alloys and Ag alloys, are also used in dentistry.

A disadvantage of using metals as biomaterials is that they are typically artificial materials and have no biofunction. Therefore, metals require additional properties before they can be used as biomaterials. Requirements for metals in medical devices are summarized in table 1. To respond to these requirements, new alloy designs and many techniques for the surface modification of metals have been researched and even commercialized.

3. Categories of research and development

Research and development of metals for medical devices or metallic biomaterials are categorized as follows:

(1) Design of new alloys
(2) Development of working processes and heat treatments
(3) Development of new surface treatment and modification techniques
  (i) Ceramic coating and growth of surface oxide
  (ii) Immobilization of functional molecules and biomolecules
  (iii) Composite with polymers
(4) Control of surface morphology
(5) Evaluation of mechanical properties
(6) Evaluation of corrosion resistance
(7) Evaluation of safety and toxicity
(8) Evaluation of biocompatibility and biofunctions
(9) Development of *in vitro* evaluation techniques

Development of new materials is performed by (1) design of alloys, (2) development of working processes, (3) surface treatment techniques and (4) control of surface morphology. In addition, (5) the evaluation of mechanical properties is necessary because good mechanical properties are essential for metals. For medical devices, (6) the evaluation of the corrosion resistance is significant. If these properties are confirmed in new materials, (7) safety and toxicity and

Table 2. Specified titanium alloys.

Composition (mass%)	Type	UNS	ASTM	ISO
Ti–3Al–2.5V	$\alpha+\beta$	R56320	ASTM B 348	–
Ti–5Al–2.5Fe	$\alpha+\beta$	–	–	ISO 5832–10
Ti–6Al–4V	$\alpha+\beta$	R56400	ASTM F 1472	ISO 5832–3
Ti–6Al–4V ELI	$\alpha+\beta$	R56401	ASTM F 136	ISO 5832–3
Ti–6Al–7Nb	$\alpha+\beta$	R56700	ASTM F 1295	ISO 5832–11
Ti–15Mo	β	R58150	ASTM F 2066	–
Ti–13Nb–13Zr	β	R58130	ASTM F 1713	–
Ti–12Mo–6Zr–2Fe	β	R58120	ASTM F 1813	–
Ti–45Nb	β	R58450	AMS 4982	–
Ti–35Nb–7Zr–5Ta	β	R58350	–	–
Ti-55.8Ni	Metallic compound	–	ASTM F 2063	–

(8) biocompatibility and biofunctions may be evaluated. Evaluation of mechanical properties and corrosion resistance is essential for metallic materials. In addition, (9) *in vitro* evaluation techniques of materials are necessary to assess the biofunction and biocompatibility of the materials without animal testing.

4. Titanium alloys

4.1. $\alpha+\beta$ type titanium alloys with large elongation

Ti and Ti alloys were developed for aerospace applications and have also been used for medical and dental implants because they show high corrosion resistance and specific strength. Their Young's modulus is about one half that of stainless steel and Co–Cr alloys, and this low Young's modulus makes them the preferred material for use in bone fixators. Ti materials form stable titanium oxide films on their surface, and their corrosion resistance is better than that of stainless steel and Co–Cr alloys as a result. Ti and most of the Ti alloys are safe for use in the human body; moreover, they exhibit good tissue compatibility, especially for hard tissue. On the other hand, they are not suitable for bone fixation wires and sternal wires that require ligatures because of their low torsion strength (torque) and torsion angle to fracture.

Ti alloys at ambient temperatures are categorized as α-type, $\alpha+\beta$-type, and β-type alloys, according to the quantities and types of their alloying elements. Many kinds of alloys have been developed (table 2), but the Ti–6Al–4V alloy, an $\alpha+\beta$-type alloy, is the most conventional one for medical use. This alloy exhibits good workability, heat treatment stability, weldability, corrosion resistance, strength and biocompatibility. The extra low interstitial (ELI) grade alloy containing small amounts of interstitial impurities, oxygen, carbon, nitrogen and hydrogen is used for biomaterials. The Ti–6Al–4V ELI alloy shows significant toughness because the impurities decrease the fatigue strength via the notch effect. The ELI alloy is used for bone fixation plates and the stems of artificial hip joints. The Ti–6Al–4V alloy has an extremely high 0.2% offset yield strength of 895 MPa, which is much higher than that of stainless steel and Co–Cr–Mo alloys, hindering plastic deformation even under high load.

The Ti–6Al–7Nb alloy [1] has been developed as a replacement for the Ti–6Al–4V alloy. This alloy was developed and is mainly used in Europe because one of its components, vanadium, shows strong cytotoxicity, although there has been no report of accidents when using Ti–6Al–4V alloy implants. The Ti–6Al–7Nb alloy has been created by substituting V with Nb at the same atomic concentration. Its corrosion resistance and safety are greater than those of Ti–6Al–4V. Elsewhere, the Ti–6Al–2.5Fe alloy developed in Europe, the Ti–13Zr–13Ta alloy (nearly β) developed in the United States, and the Ti–6Al–2Nb–1Ta and Ti–15 Zr–4Nb–4Ta alloys developed in Japan have been standardized. These are $\alpha+\beta$ type alloys.

Materials scientists and engineers understand that the fracture of metallic materials can be avoided when the materials have sufficient fatigue strength and corrosion resistance. However, recently, the lower elongation of $\alpha+\beta$ type Ti alloys than that of stainless steel has caused an 'artificial fracture' or 'human error' in spinal fixators and maxillofacial plates because the elongation to fracture of $\alpha+\beta$ type Ti alloys is only about 10–17%. The following four causes of fracture of metals are feasible in medicine: (i) larger plastic deformation than the elongation to fracture is applied by medical doctor at the operation site, (ii) multiple plastic deformation is applied if the first bending by the doctor at the operation site is unsuccessful, (iii) alloy fatigue and (iv) large crevices as a result of corrosion initiate fracture.

Causes (i)–(iv) are illustrated in figure 1. The phenomena described in (i) and (ii) may occur as a result of mismanaging the material when its elongation and hardening are miscalculated, whereas those described in (iii) and (iv) can be prevented by improving the mechanical and electrochemical properties of the material. To prevent fractures such as those described in (i) and (ii), specific training of medical professionals is required to understand the relationship between the fracture and elongation and work hardening. In addition, the development of $\alpha+\beta$ type Ti alloys having large elongation and sufficient strength is required. However, no optimal Ti alloy has been developed so far.

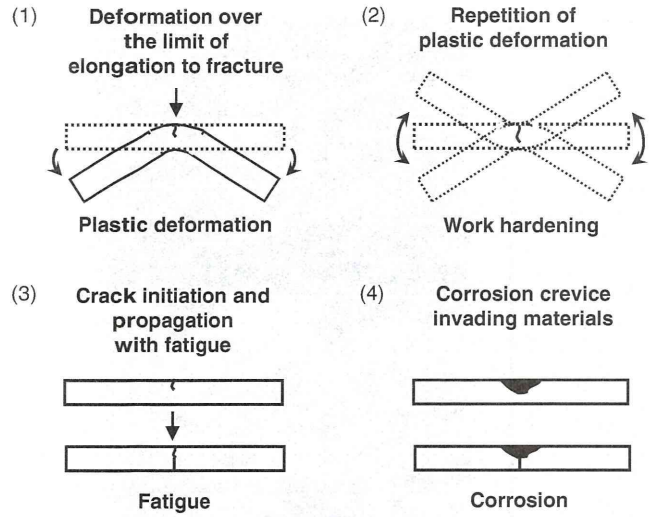

Figure 1. Causes of fracture of metals in medicine: (i) larger plastic deformation than the elongation to fracture is applied by medical doctor at the operation site; (ii) multiple plastic deformation is applied if the first bending by the medical doctor at the operation site is unsuccessful; (iii) alloy fatigue; (iv) large crevices as a result of corrosion work initiate fracture.

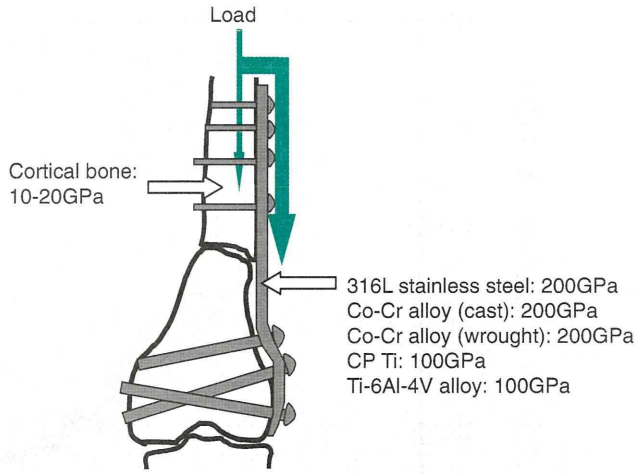

Figure 2. When fractured bone is fixed with a metallic bone fixator, such as a bone plate and screws and bone nail, the load to the fixation part during healing is mainly received by the metallic fixators because of the difference in the Young's moduli.

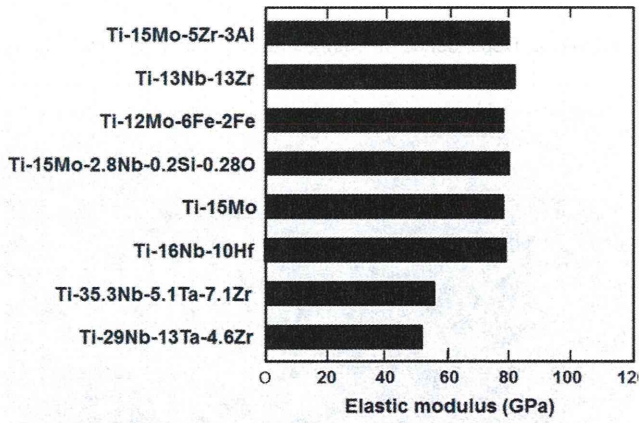

Figure 3. Elastic moduli of β-type alloys [4].

4.2. β type titanium alloys and porous titanium with small Young's modulus

The Young's modulus of metallic materials is higher than that of cortical bone: it is about 200 GPa in stainless steels and Co–Cr–Mo alloys, about 100 GPa in Ti and Ti alloys, and 10–20 GPa in cortical bone. When fractured bone is fixed with a metallic bone fixator, such as bone plate and screws and bone nail, during healing, a load to the fixation part is mainly received by metallic fixators because of the difference in their Young's modulus, as shown in figure 2, inducing device-related osteoporosis or osteopenia. This phenomenon is well known as 'stress shielding' in orthopedics. This high Young's modulus generates other problems. When a metal is used as a metallic spacer in spinal fixation, the spacer is mounted in bone. In the case of a dental implant, occlusal pressure is not absorbed by the implant and directly conducted to the jaw bone.

To solve these problems, metals with low Young's modulus are required. Two approaches are feasible: decrease Young's modulus of the metal itself or decrease the apparent Young's modulus by forming a porous body.

The requirement for a low Young's modulus to prevent stress shielding in bone fixation is fulfilled by β-type alloys, in which the Young's modulus may decrease to about 60 GPa. Various β-type alloys, Ti–12Mo–6Zr–2Fe [2] and T–15Mo [3], have been developed in the United States, and the Ti–15Mo–5Zr–2Al alloy has been specified. The mechanical properties of β-type alloys are shown in figure 3 [4]. Ti alloys consisting of elements with low toxicity have been developed. The basic design of the alloys is the substitution of V and Al with Nb, Ta, Zr and Hf, which belong to the groups 4 and 5 of the periodic table; for this reason, Ti–29Nb–13Ta–4.6Zr has been developed as a β-type alloy [5]. This alloy is transformed to the β phase by heat treatment and forging and shows the lowest Young's modulus among β-type alloys. Elsewhere, the Ti–Nb–Sn alloy system is in the process of development [6].

Figure 4 shows the dependence of the elastic modulus of Ti porous body on porosity [7]. The pores are sometimes filled by polymers to adjust the apparent Young's modulus during bone healing. Ultrahigh-molecular-weight polyethylene (UHMWPE) [8] and poly(methyl methacrylate) (PMMA) [9] are used to fill the pores in porous Ti. Figure 5 shows porous Ti with pores filled by UHMWPE.

4.3. Nickel-free titanium-based superelastic alloy

Ti–Ni alloys consisting of equal atomic amounts of Ti and Ni (49–51 mol% Ni) show unique mechanical properties, such as shape memory, superelasticity and efficient damping. Because of the superelasticity, the Ti–Ni alloy is used for guide wires, stents, orthodontic arch wires, endodontic reamers and files.

Recently, early-stage fractures of stents in service have been reported. Among self-expanding Ti–Ni femoral stents, 37.2% (45 of 121) fractured within 10.7 months of implantation, as detected by x-ray examination (figure 6) [10].

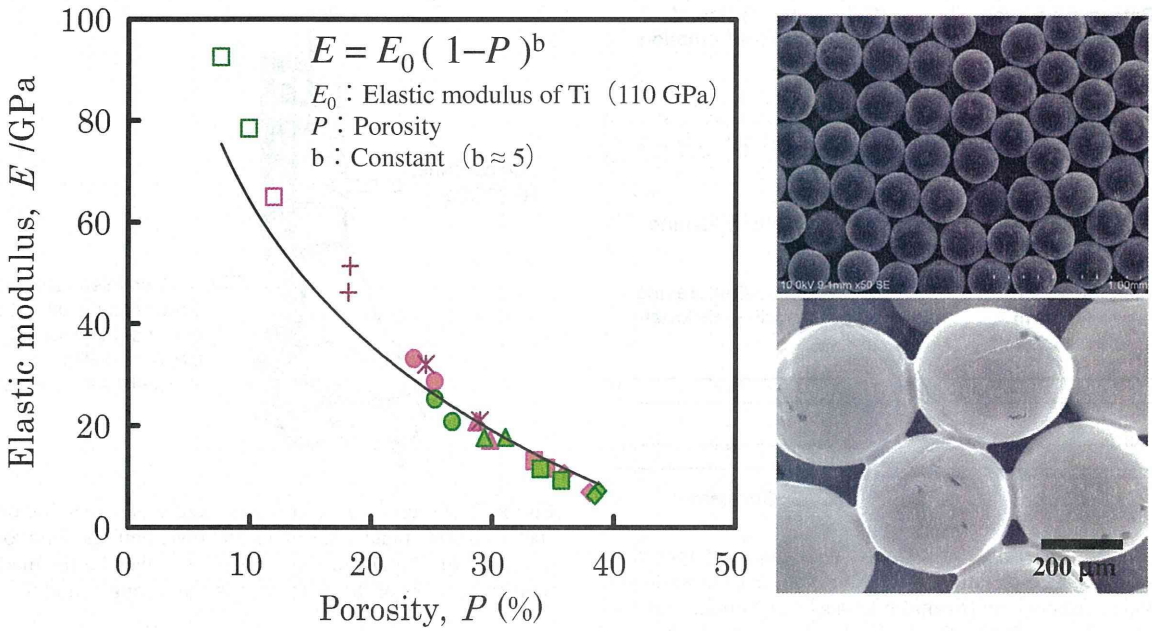

Figure 4. Dependence of Young's modulus of Ti porous body on porosity (left) and scanning electron photographs of porous Ti (right).

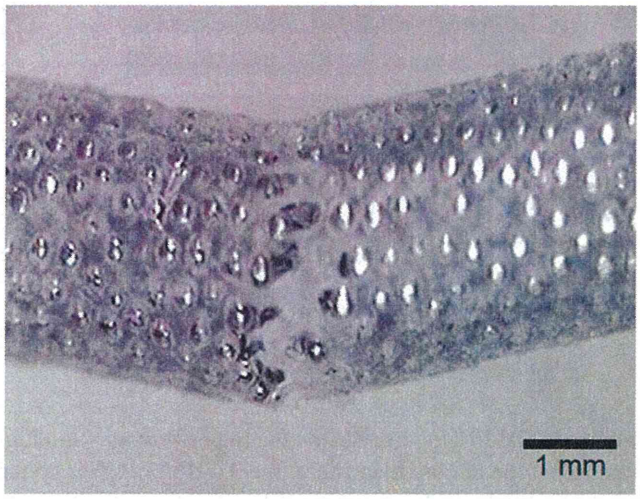

Figure 5. Porous Ti body in which the pores are filled with ultrahigh-molecular-weight polyethylene.

In drug-eluting stents, all fractures occurred around areas of increased rigidity due to the overlapping of metals, which may have formed a fulcrum for metal deformation due to vessel movement [11]. Ti–Ni stents implanted for suboptimal angioplasty in the superficial femoral artery tend to fracture [12]. Coronary stent fractures with shear bonding forces result from cardiac contractions [13]. In addition, stent fractures after percutaneous coronary intervention with sirolimus-eluting stents have been reported 2 days after stent implantation [14]. On the other hand, the tensile strength and fatigue strength of stainless steels are sufficient; thus, the fractures might originate from improper stent design. Stents consisting of Ti–Ni alloys must be carefully designed to avoid fractures during service. In particular, during expansion, unexpectedly high local deformation may generate fractures.

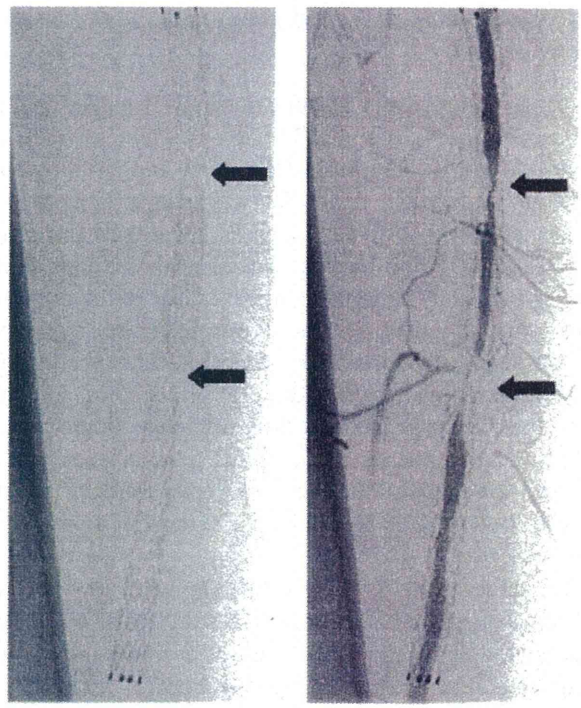

Figure 6. Early-stage fractures of self-expanding Ti–Ni femoral stents in service observed by x-ray examination [10].

The fatigue and fracture mechanisms of the superelastic Ti–Ni alloy have been only partly elucidated [15–17].

On the other hand, severe pitting and crevice corrosion are observed in Ti–Ni alloys in stent grafts [18–20], as shown in figure 7 [18]. These problems may occur in Ti–Ni alloys and stainless steel at crevices between an artificial blood vessel and a metallic stent because of the electrochemical properties of the alloys. Fracture may then initiate at corroded sites. Alloys that are resistant to pitting and corrosion must be

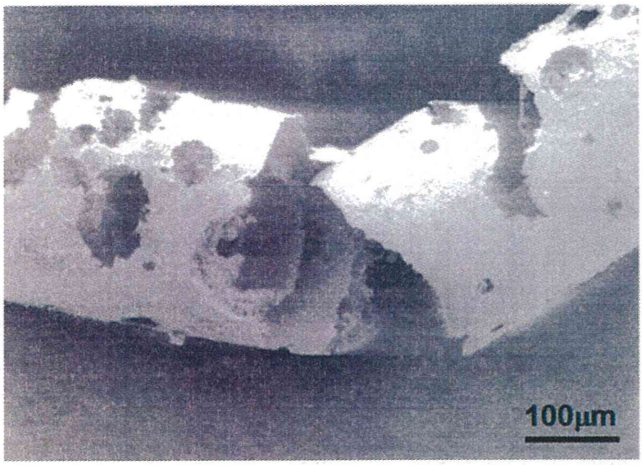

Figure 7. Severe pitting and crevice corrosion observed in Ti–Ni alloys in stent grafts [18].

developed and used. The safety and durability of Ti–Ni alloys as stent and stent graft materials are not guaranteed because of their severe corrosion and unknown fatigue properties.

The use of Ti–Ni alloy with about 50 mol% Ni in medicine is limited by safety. Therefore, there is a great demand for Ni-free shape-memory and superelastic alloys to solve such problems. Ti–Sn–Nb [21], Ti–Nb–Al [22], Ti–Mo–Ga [23], Ti–Mo–Sn [24], Ti–Nb–O [25], and Ti–Nb–Zr [26] alloy systems exhibit shape-memory effect and superelasticity, while the recovery strain and superelastic deformation stress of these alloys are still lower than those of the Ti–Ni alloy. It is possible to improve the shape-memory effect and superelasticity by adjusting the alloy composition and working heat treatment.

5. Bioabsorbable metals

Common metals used for stents are not bioabsorbable but remain in the vessel semipermanently. To eliminate a stent material after service, it is sometimes preferable to use bioabsorbable materials; however, only polymeric bioabsorbable materials are currently available. Another application of absorbable metals is as bone fixators that should also be eliminated after bone healing. Currently, there are two candidates for bioabsorbable metallic materials: magnesium alloy [27, 28] and pure iron [29].

Stents made of biodegradable Mg alloy are safe [28] but associated with a modest degree of neointima formation and late recoil. Mg is a bioessential element, even though it is corrosive in an aqueous environment. Because the control of absorbance, *i.e.* corrosion, of Mg in the human body, is difficult due to the extreme activity of Mg, alloying is absolutely necessary to control the corrosion rate. In addition, hydrogen evolution occurs when Mg is dissolved and a gas cavity is formed during the implantation of Mg alloys [30]. Control of the corrosion rate for safety in the human body is a key factor in the utilization of Mg alloys for medical devices. Efforts to achieve this purpose are currently underway [27].

6. Nickel-free austenitic stainless steel

Nitrogen (N), which is one of the austenitizing elements, is an important alloying element in austenitic stainless steels in terms of corrosion resistance and strength [31]. Nitrogen dissolved in austenitic stainless steel improves its strength resistance to pitting corrosion and crevice corrosion in solutions containing chloride ions. The related mechanisms are summarized as follows [32]:

(1) N in solid solution produces NH_4^+, hindering oxidation inside a pit;
(2) Concentrated N at the passive film/alloy surface stabilizes the film and prevents the attack by anions (Cl^-);
(3) Nitrate ions are produced to improve resistance to pitting corrosion;
(4) N addition stabilizes the austenitic phase; and
(5) N blocks kinks and controls the increase of electric current for pit production.

Therefore, austenitic high-nitrogen stainless steels containing over 0.3 wt% N have been developed. On the other hand, Ni-free austenitic stainless steels have been designed where Ni is replaced by N and Mn; such steels show high strength and corrosion resistance [33]. The Fe–(19–23)Cr–(21–24)Mn–(0.5–1.5)Mo–(0.85–1.1)N alloy (BioDur® 108) in the United States [34], the Fe–18Cr–18Mn–2Mo–0.9N alloy in Germany [35] and the Fe–(15–18)Cr–(10–12)Mn–(3–6)Mo–0.9N alloy in Switzerland [36] have been developed for medical use. These alloys are fabricated with an electrical slug-remelting process whereby N is absorbed in the alloy during melting under a high-pressure N_2 atmosphere. A new manufacturing process has been developed, in which N is absorbed into ferritic stainless steel after forming at 1200 °C [37].

7. Low magnetic susceptibility alloys for MRI

Magnetic resonance imaging (MRI) is widely used as an important diagnostic tool, especially for orthopedic and brain surgery. This method has remarkable advantages for obtaining various cross-sectional views and for diagnosis of the human body with no invasion and no exposure of the human body to x-ray radiation. However, MRI diagnosis is inhibited when metals are implanted in the body, since metallic implants, such as stainless steels, Co–Cr alloys and Ti alloys become magnetized in the intense magnetic field of the MRI instrument, and artifacts occur in the image [38, 39]. Such artifacts can disturb the images of organs and tissues around the implant, preventing exact diagnosing. The area affected by the artifacts is related to the magnetic susceptibility of the implants [40–42] and decreases with decreasing magnetic susceptibility. Operations under open MRI conditions require devices with low magnetic susceptibility. Therefore, metals with low magnetic susceptibility should be developed as MRI continues to increase in popularity.

A concept for the development of alloys with low magnetic susceptibility is shown in figure 8. Figure 8(a) presents a method of alloying a paramagnetic metal with

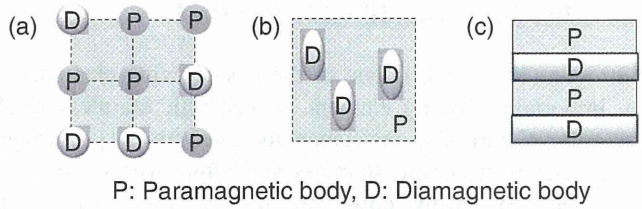

Figure 8. Concept of the development of alloys with low magnetic susceptibility. Alloying paramagnetic metal with diamagnetic metal (a), precipitation of a diamagnetic or low magnetic susceptibility phase in a paramagnetic matrix phase (b), and formation of composite of paramagnetic metal and diamagnetic material (c).

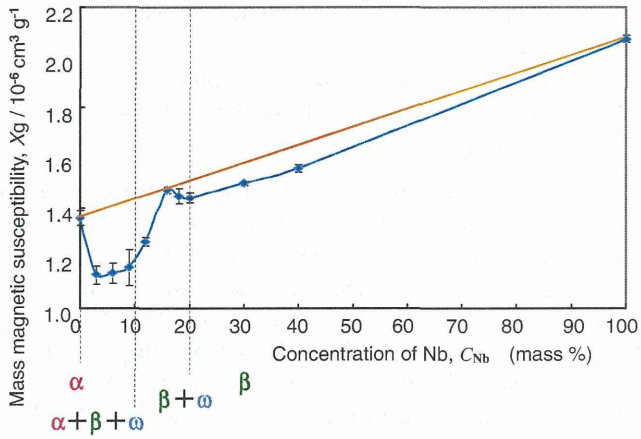

Figure 9. Effects of Nb content and constituent phases on the magnetic susceptibility of Zr–Nb alloy.

diamagnetic metal. In this sense, the magnetic susceptibility of a Au–Pt–Nb alloy is similar to that of water [43]. Figure 8(b) outlines a technique to precipitate a diamagnetic or low magnetic susceptibility phase in a paramagnetic matrix phase. This technique is explained below. Finally, figure 8(c) illustrates a technique to form a composite of paramagnetic metal and diamagnetic material that is proven both theoretically and empirically [44].

To reduce artifacts in the second technique mentioned above, Ti–Zr, Zr–Nb, and Zr–Mo alloys with low magnetic susceptibility have been developed. The magnetic susceptibility of the Zr–Nb alloy is shown in figure 9; it exhibits minimum values where the ω phase is formed. The magnetic susceptibility was reduced in Zr–Nb and Zr–Mo alloys up to about one-seventh of that of the Co–Cr–Mo alloy and one-third of that of Ti and Ti alloys [45–47], as shown in figure 10. Among Zr-based alloys, Zr–9Nb and Zr–3Mo possess low magnetic susceptibility owing to the contribution of the ω phase in their structure, as shown in figure 11. The magnetic susceptibilities of the α, β, and ω phases in Zr-based alloys obey the relation $\chi_\omega < \chi_\alpha < \chi_\beta$ [46, 47]. Although Zr–3Mo and Zr–9Nb alloys have low magnetic susceptibilities, it is difficult to apply plastic deformation to these alloys during processing for medical devices because their tensile strength and elongation are limited by the ω phase [48]. The ω phase is categorized into isothermal ω, athermal ω and strain-induced

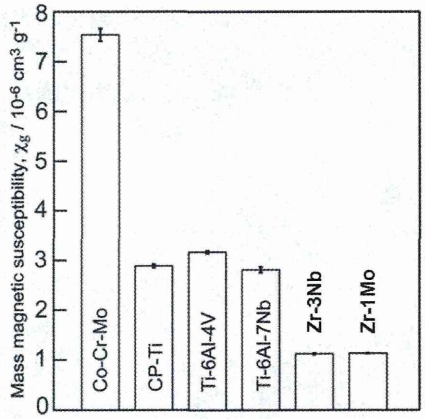

Figure 10. Magnetic susceptibilities of metals used for medical devices and Zr–Nb and Zr–Mo alloys.

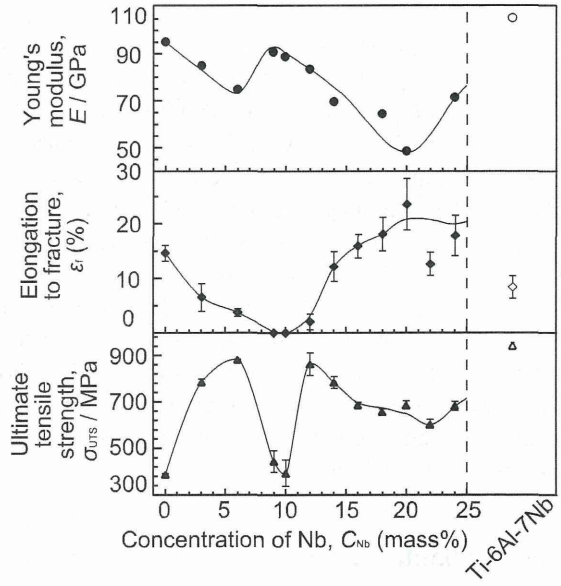

Figure 11. Mechanical properties of Zr–Nb alloys versus Nb content.

ω phases depending on the formation processes [49]. The isothermal ω phase is formed during heat treatment; it causes hardening and embrittlement [50–52] and decreases the magnetic susceptibility of the alloy. The athermal ω phase is martensitically formed on quenching from the β phase region to room temperature and also contributes to lowering the magnetic susceptibility [46, 47]. The strain-induced ω phase is formed by applying plastic deformation and appeared in the series of Ti-based alloys consisting of the metastable β phase, such as Ti–Cr, Ti–Mo, and Ti–V alloys [53–55]. The phase constitutions of Zr–Nb alloys are similar to those of the above-mentioned alloys, and the formation of the strain-induced ω phase can be expected in the Zr–14Nb alloy consisting of the metastable β phase [48]. Therefore, the magnetic susceptibility of Zr–Nb alloys can be reduced by applying plastic deformation because of the formation of the strain-induced ω phase.

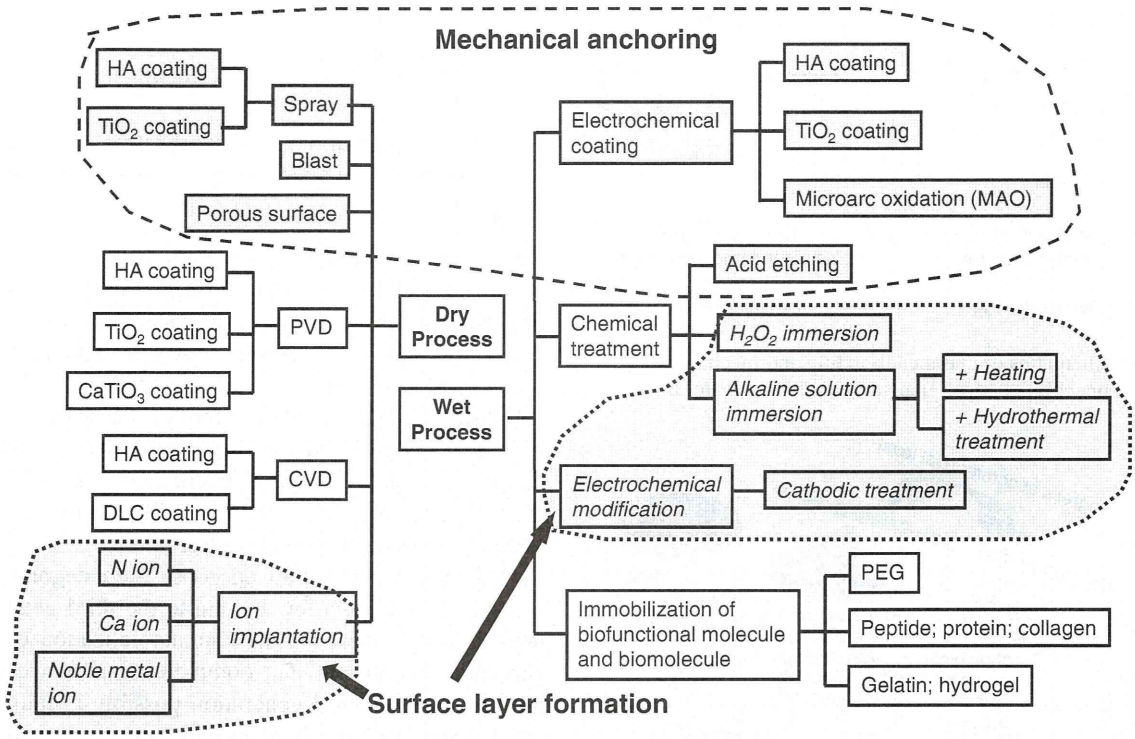

Figure 12. Surface modification techniques by both dry and wet processes used in research and industry.

8. Surface modification of metallic biomaterials

A disadvantage of using metals as biomaterials is that they are typically artificial materials and have no biofunction. To add biofunction to metals, surface modification is necessary because a biofunction cannot be added during manufacturing processes such as melting, casting, forging and heat treatment. Surface modification is a process that changes a material's surface composition, structure and morphology, leaving the bulk mechanical properties intact. With surface modification, the tissue compatibility of the surface layer can be improved. Dry processes and wet processes are conventional and predominant surface modification techniques. Figure 12 summarizes the surface modification techniques by both dry and wet processes used in research and industry. Surface modification techniques are reviewed elsewhere [56, 57].

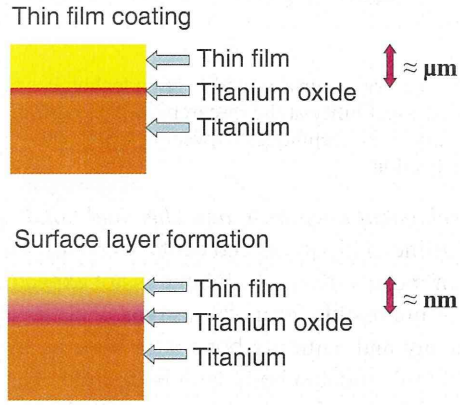

Figure 13. Research to improve hard-tissue compatibility involves two approaches based on the resultant surface layer: a calcium phosphate layer with the thickness in the micrometer scale and a surface-modified layer with the thickness in the nanometer scale.

8.1. Surface treatment for bone formation

8.1.1. Current techniques. Ti and its alloys, which show good hard tissue compatibility, are used for dental implants and artificial hip joints. However, the hard-tissue compatibility of these materials is lower than that of bioactive ceramics, such as hydroxyapatite and bioactive glasses. Therefore, numerous surface modification techniques to improve the hard tissue compatibility of Ti have been developed, and some have been commercialized. Research to improve hard-tissue compatibility involves two approaches based on the resultant surface layer: a calcium phosphate layer with the thickness in the micrometer scale and a surface-modified layer with the thickness in the nanometer scale, as shown in figure 13.

In the former case, currently, plasma spraying of apatite on metallic materials is widely used to form the apatite layer. In the case of plasma-sprayed apatite, however, the apatite–Ti interface or the apatite itself may fracture under relatively low stress because of low interface bonding strength and low toughness of the sprayed layer. To overcome this weakness, dynamic ion mixing is applied to form an apatite with high interface bonding strength.

In the latter case, hard-tissue compatibility can be improved by modifying the Ti surface instead of the apatite coating. Many surface modification techniques have been developed that involve neither a hydroxyapatite coating nor a calcium phosphate coating.