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Low Modulus Titanium Alloys for Inhibiting Bone Atrophy

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1. Introduction

Metallic biomaterials constitute approximately 70% - 80% of all implant materials, and thus represent a very important class of biomaterials. Among the various metallic biomaterials such as stainless steels and Co-Cr alloys, titanium and its alloys exhibit the best biocompatibility. Consequantly, titanium and its alloys have been the fucus of attension for biomedical materials, especially for use in load bearing implants such as artificial hip joints, bone plates and screws, spinal instruments, and dental implants.

The Young's moduli of metallic biomaterials are generally much higher than that of the human cortical bone (hereafter, bone) (Niinomi, 2002a). If the Young's modulus of a load bearing implant made of metallic biomaterials is higher than that of the cortical bone, bone atrophy occurs because of the stress shielding between the implant and bone (Sumitomo, 2008). Stress shielding causes loosening of the implants such as artificial joints or bone re-fracture after extraction of the implants. Therefore, the Young's modulus of the metallic biomaterials must be equal to that of the natural bone. Titanium and its alloys possess lower Young's moduli than those of other mettalic biomaterials such as stainless steels and Co-Cr alloys. β-type titanium alloys, in particular, having a single β phase exhibit much smaller Young's moduli compared with α- and (α + β)-type titanium alloys (Niinomi, 2002b). As such, the β-type titanium alloys are particulary promissing for biomedical applications. A number of β-type titanium alloys composed of non-toxic and non-allergic elements with low Young's modulus have been developed and even more are currently under development (Niinomi, 2011a). Much of the current research in the biomaterials field has been directed at lowering the Young's modulus of the β-type titanium alloys for biomedical applications.

The mechanical biocompatibility factors such as fatigue strength, fretting fatigue strength, tensile properties, wear resistance, fracture toughness, etc., including the Young's modulus are very important factors for the practical application of the allloys in biomaterials as well as the biological biocompatibilities (Niinomi, 2008a). Among the mechanical biocompatibility factors, the endurance, i.e., the fatigue strength is one of the most important factors (Niinomi, 20007). The development of metallic biomaterials with improved fatigue strength and a simaltaneously low Young's modulus is desirable for biomedical applications.

The effect of the Young's modulus of the metallic implant should be clarified by animal experiments prior to medical applications, and recently, these kinds of studies have begun to be implemented (Niinomi, 2002b).

A recent report highlited the contrasting requirements of patients versus surgeons for metallic implants. The rquirements of the patients dictate that the implants have a Young's modulus similar to that of the bone, whereas while the surgeons require a high Young's modulus for inhibiting springback both during and after the operation procedure (Nakai, 2011a). Titanium alloys that simultaneously satisfy the demands of both patients and surgeons are thus necessiated.

There is a demand to remove the implant when the bone fracture is healed, in which case, the adhesion of the implant to the bone must be weak enough to inhibit the refracture of the bone. This requires titanium alloys having poor bone conductivity, but excellent biocompatibility (Zhao, 2011).

This chapter introduces low modulus β-type titanium alloys and various methods of lowering the Young's modulus of the β-type titanium alloy, improving the strength and fatigue strength of the β-type titanium alloy while maintaining a low Young's modulus, the evaluation of the effect of the Young's modulus on bone atrophy using rabbits, titanium alloys with variable Young's moduli, and removable titanium alloys are described.

2. Low modulus β–type titanium alloys for biomedical applications

A number of β-type titanium alloys with low Young's modulus have been developed for use in the human body. The titanium alloys composed of safe alloying elements developed to date include the following; Ti-13Nb-13Zr, Ti-12Mo-6Zr-2Fe, Ti-15Mo, Ti-15Mo-5Zr-5Sn, Ti-15Mo-5Zr-3Al, Ti-16Nb-10Hf, Ti-15Mo-2.8Nb-0.2Si, Ti-30Ta, Ti-35Zr-10Nb, Ti-8Fe-8Ta, Ti-8Fe-8Ta-4Zr, Ti-35Nb-7Zr-5Ta, Ti-29Nb-13Ta-4.6Zr (TNTZ), and Ti-Nb-Sn system alloys (Niinomi, 2011a). Shape memory and super-elastic Ti-Nb based alloys have been also been developed; Ti-Nb, Ti-Nb-O, Ti-Nb-Sn, Ti-Nb-Al, Ti-22Nb-(0.5-2.0)O (at%),Ti-Nb-Zr, Ti-Nb-Zr-Ta, Ti-Nb-Zr-Ta-O, Ti-Nb-Ta-Zr-N, Ti-Nb-Mo, Ti-22Nb-6Ta(at%), Ti-Nb-Au, Ti-Nb-Pt, Ti-Nb-Ta, and Ti-Nb-Pd system alloys. Ti-Mo based alloys have been developed; Ti-Mo-Ga, Ti-Mo-Ge, Ti-Mo-Sn, Ti-Mo-Ag, Ti-5Mo-(2-5)Ag (at%), Ti-5Mo-(1-3)Sn (at%), in addition to Ti-Sc-Mo system alloys. The Ti-Ta based alloys are Ti-50Ta, Ti-50Ta-4Sn, and Ti-50Ta-10Zr. Other alloys such as Ti-7Cr-(1.5, 3.0, 4.5)Al super elastic and shape memory alloys, Gum Metal (Ti-25at% (Ta, Nb, V) + (Zr, Hf, O)), and Ti-9.7Mo-4Nb-2V-3Al super elastic alloys have also been developed (Niinomi, 2011b).

3. Further decreases in Young's modulus

Improvements in the static strength of biomaterials such as the tensile strength can be achieved by employing strengthening mechanisms including work hardening, grain refinement strengthening, precipitation strengthening, and dispersion strengthening. One of the best ways to increase tensile strength while maintaining a low Young's modulus is to introduce a number of dislocations into the alloy system by conventional severe cold working techniques such as severe cold rolling and swaging, and by special severe cold working techniques such as high pressure torsion (HPT), accumulated roll-bonding (ARB) and equal channel angular pressing (ECAP) (Yilmazer, 2009).

Figure 1 (Niinomi, 2010a) shows the relationships between the tensile properties and working ratio of Ti-29Nb-13Ta-4.6Zr (TNTZ) while Fig. 2 (Niinomi, 2010a) shows the relationship between the Young's modulus and working ratio of TNTZ after subjecting TNTZ to severe cold working by general severe cold rolling or swaging in both cases.

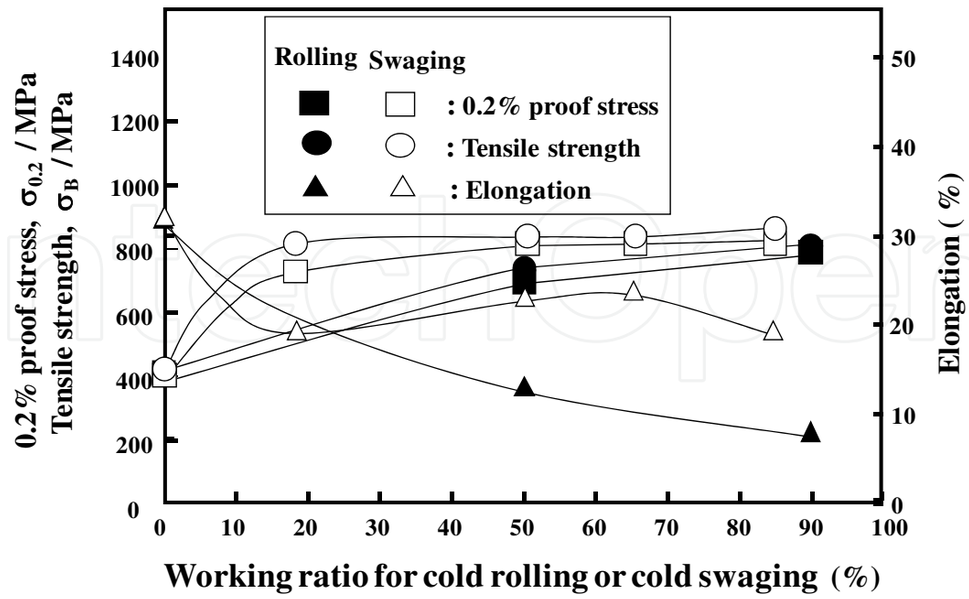


Fig. 1. Tensile properties of TNTZ subjected to cold rolling or cold sawaging as a function of working ratio.

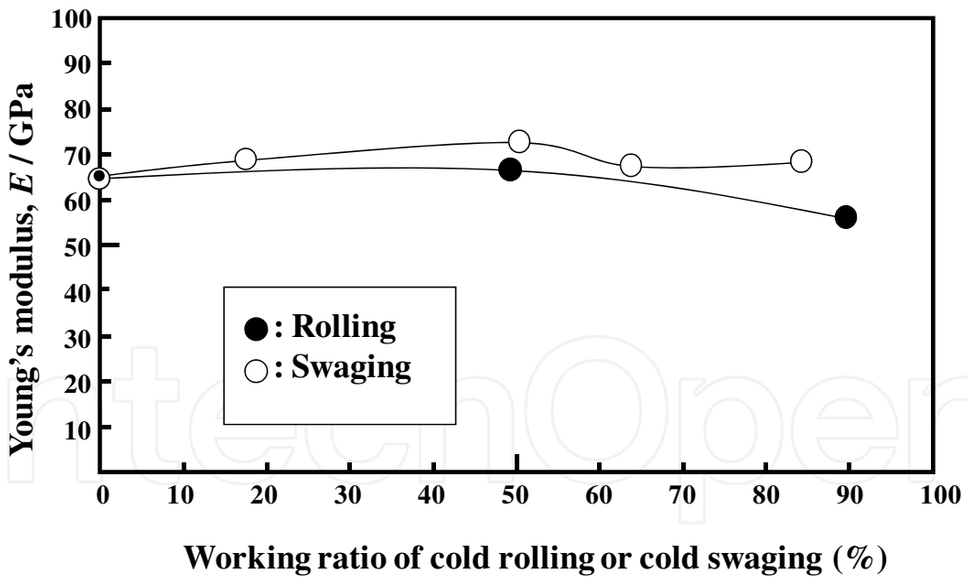


Fig. 2. Young's modulus of TNTZ subjected to cold rolling or cold swaging as a function of working ratio.

The tensile strength and 0.2% proof strength of cold rolled and swaged TNTZ increase with increasing working ratio up to approximately 20 % and then become almost constant. The ductility (elongation) of cold rolled TNTZ decreases with increasing cold working ratio, but that of swaged TNTZ decreases with increasing cold working ratio up to approximately 20 % and then becomes constant while maintaining high elongation. The tensile and 0.2 %

proof stress of TNTZ subjected to cold rolling and swaging are nearly equal to those of Ti-6Al-4V extra-low interstitial alloy (Ti-6Al-4V ELI); having a tensile strength of around 800 MPa) at high cold working ratio with good elongation.
The Young's modulus of TNTZ subjected to cold rolling or cold swaging is almost constant with increasing working ratio. The Young's modulus of TNTZ subjected to cold rolling tends to decrease when the working ratio is high because the trend of the formation of the texture becomes significant.

3.1 Lowering the Young's modulus by control of the crystal direction

Anisotorophy of the mechanical properties of β-type titanium alloy, TNTZ, has been reported to be significantly larger than those of other metallic materials such as carbon steel, S45C. Figure 3 (Niinomi, 2008b) shows the tensile strain (ε) versus lattice strain (ε_l) of TNTZ and ferrite in S45C, both of which have the bcc structure. Strains were calculated from the (110), (200), and (211) planes of the β phase of TNTZ and ferrite in S45C from the XRD profiles, obtained from in-situ X-ray analysis under tensile loading. The degree of the change in lattice strain with tensile strain for S45C is smaller than that for TNTZ. The relationship between the lattice strain and tensile strain obtained from the (100), (200), and (211) planes is nearly the same for each plane in S45C, but varies significantly for TNTZ. This illustrates that the anisotropy of the mechanical properties of TNTZ is large. Based on this trend in mechanical properties, the Young's modulus of TNTZ is considered to exhibit large anisotprophy. The single crystal of TNTZ, which grows to a certain direction, is expected to exhibit a low Young's modulus.

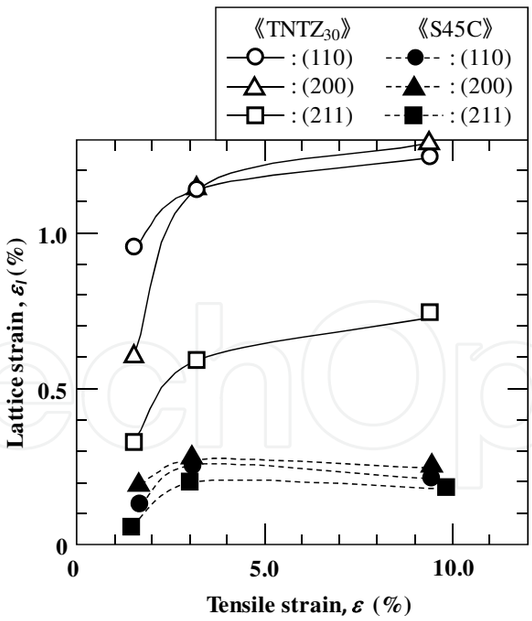


Fig. 3. Relationships between tensile strain and lattice strain calculated using several diffraction angles of $TNTZ_{30}$ (Ti-30Nb-10Ta-5Zr) and carbon steel (S45C).

Figure 4 (Tane, 2008) shows the orientation dependence of the Young's modulus in Ti-29Nb-Ta-Zr and Ti-25Nb-Ta-Zr single crystals between the <100> and <110> directions, which were calculated by coordinate conversion of c_{ij}. The symbol θ denotes the angle from the

<100> direction on the <110> zone axis. The Young's modulus of Ti-29Nb-Ta-Zr is lower than that of Ti-25Nb-Ta-Zr in all directions, but there are many common features independent of the alloy composition. The Young's modulus of both single crystals shows anisotropy as a function of θ; the Young's modulus of both crystals in the <100> direction, E_{100}, is approximately two times lower than the Young's modulus in the <111> direction, E_{111}, where E_{100} and E_{111} are the lowest and highest among all of the Young's moduli in all the directions, respectively. The lowest Young's modulus, E_{100}, of the Ti-29Nb-Ta-Zr single crystal is quite low at a value of only about 35 GPa, which is comparable to that of cortical bone. This level may be effective in the suppression of stress shielding in bone. Therefore, metallic single crystals of titanium alloys may be applicable as biomaterials; these may be referred to as "single crystal biometals".

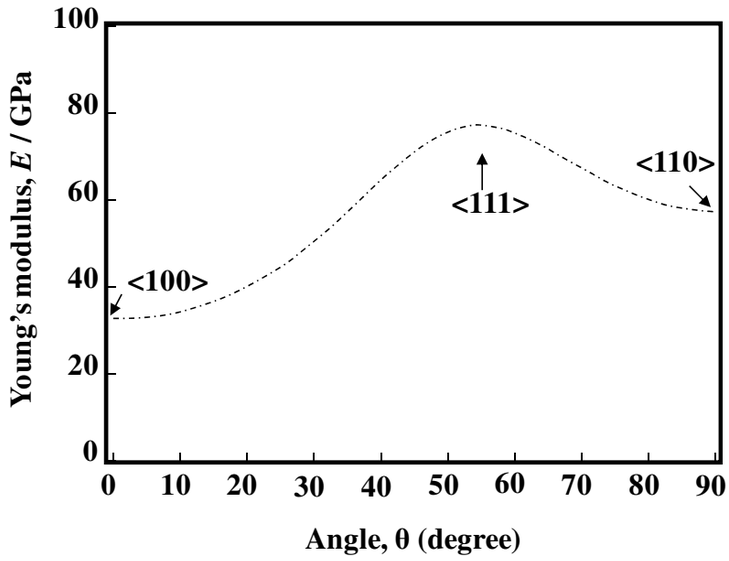


Fig. 4. Young's modulus of single-crystal Ti-29Nb-13Ta-4.6Zr in directions between [100] and [110].

3.2 Lowering the Young's modulus through structural design

Introduction of porosity into titanium and its alloys is a very effective method for further reducing the Young's moduli of titanium and its alloys. Introduction of porosity into titanium may affect a drastic reduction of the Young's modulus, and offer control of the Young's modulus by variation of the porosity. The relationship between the Young's modulus and porosity of porous titanium made from titanium powders with different particle diameters have been compared with the Young's modulus of bulk titanium in a recent report. According to that report, at a porosity of approximately 30%, the Young's modulus is nearly equal to that of cortical bone. The use of a titanium alloy with an even lower Young's modulus than titanium may allow for the achievement of a Young's modulus equal to that of cortical bone at lower porosity compared with the case of titanium. Pores of the proper size also enhance the bone conductivity. On the other hand, however, increasing the porosity of titanium results in a drastic decrease in its strength. At a porosity of approximately 30%, which leads to the Young's modulus equal to that of cortical bone,the 0.2% proof stress is below 100 Mpa (Oh, 2002).

This decrease in the strength of porous titanium can be prevented by combining with a biocompatible polymer. Penetration of the polymer into the porous titanium can be achieved by pressing. In the pressing method, HMDP (high molecular density polyethylene) is pressed into porous titanium.

Another proposed method for penetration of a polymer into the titanium pores (Nakai, 2010) involves firstly using the monomer of PMMA. The porous titanium (pTi) is first immersed into a monomer solution of PMMA leading to penetration of the monomer into the pores of titanium. The PMMA monomer in the porous titanium is then subjected to polymerization by heating. By combination with PMMA, the strength of porous titanium increases as shown in Fig. 5 (Nakai, 2010). The tensile strength of PMMA infiltrated porous titanium is greater than that of porous titanium, whereas the Young's modulus of PMMA infiltrated porous titanium is nearly equal to that of porous titanium as shown in Fig. 6 (Nakai, 2010). The tensile strength of PMMA infiltrated porous titanium increases by silane coupling treatment while the Young's modulus remains unchanged as shown in Figs. 5 and 6.

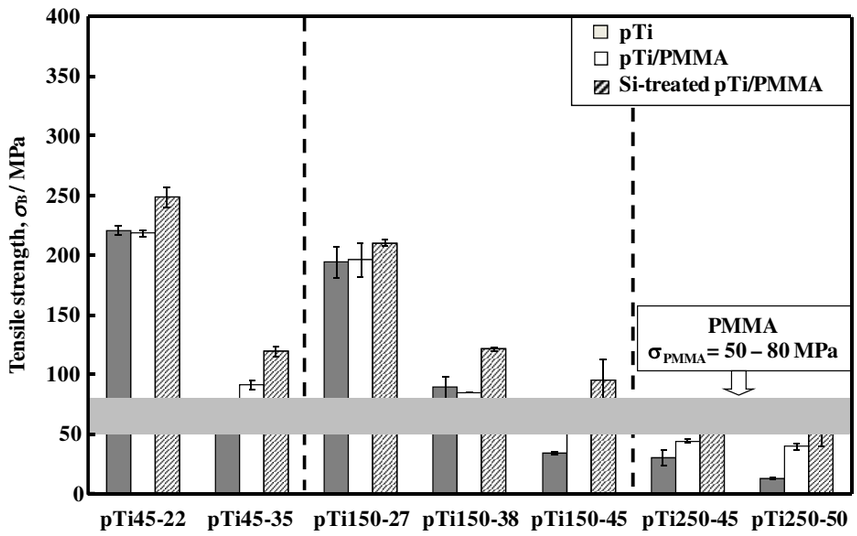


Fig. 5. Tensile strengths of pTi, pTi/PMMA, and Si-treated pTi/PMMA.

Another advantage offered by porous titanium and polymer composites is the ease with which bio-functionalities may be added given that the surface of porous titanium can be covered with polymers. Instead of PMMA, biodegradable PLLA can also be filtrated into the pores of porous titanium by modifying the process for PMMA filtration. Fig. 7 (Nakai, 2011b) shows the compressive 0.2% proof stress of porous titanium and PLLA infiltrated porous titanium as a function of porosity in the range of 5%–45%. In this figure, the compressive 0.2% proof stress of PLLA obtained experimentally is also shown for comparison. The compressive 0.2% proof stress of PLLA infiltrated porous titanium is higher than those of porous titanium independent to porosity. This result indicates that the PLLA filling can improve the compressive 0.2% proof stress of porous titanium at any degree of porosity. In particular, the increase in compressive 0.2% proof stress due to PLLA filling is relatively large for porosities higher than or equal to 35%. The compressive 0.2% proof stress of PLLA obtained is around 80–120 MPa, which is higher than that of PMMA (around 50–80MPa) (Honda, 1961; Imai and Brown, 1976).

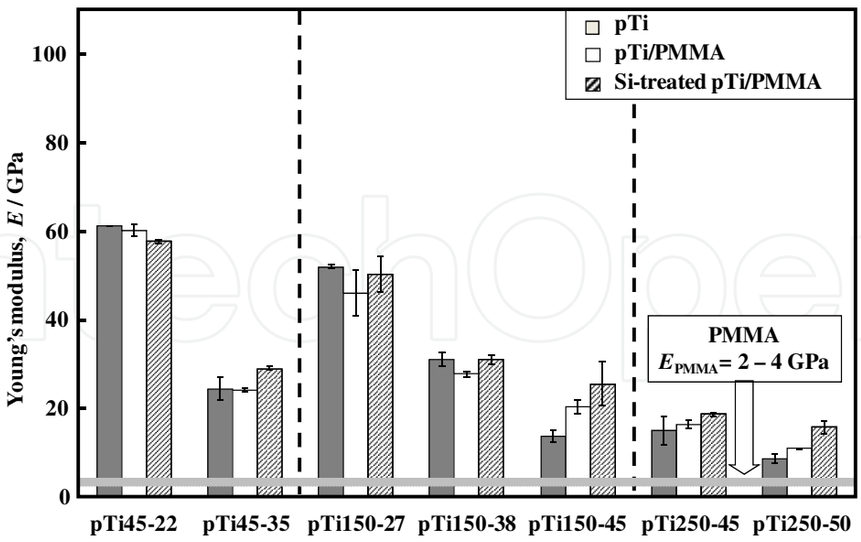


Fig. 6. Young's moduli of pTi, pTi/PMMA, and Si-treated pTi/PMMA.

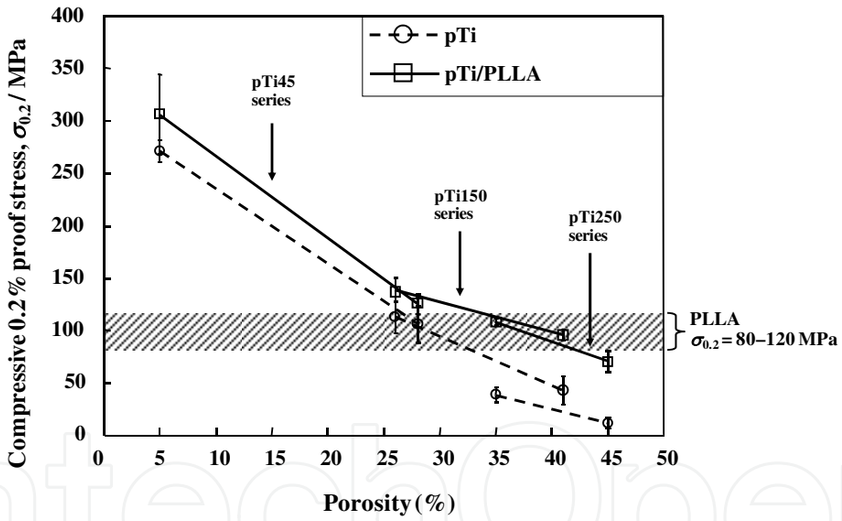


Fig. 7. Compressive 0.2% proof stresses of porous titanium (pTi) and porous titanium filled with poly-L-lactic acid (pTi/PLLA).

Figure 8 (Nakai, 2011b) shows the compressive Young's modulus of porous titanium and PLLA infiltrated porous titanium as a function of porosity in the range of 5%–45%. In this figure, the compressive Young's modulus of PLLA obtained experimentally is also shown for comparison. The compressive Young's modulus of porous titanium decreases with increasing porosity. The compressive Young's modulus is higher for PLLA infiltrated porous titanium than for porous titanium with a relatively high porosity of ≥35%.

Since PLLA is biodegradable, an agent to enhance the bone conductivity can be added to the PLLA in the porous titanium, and the agent can then be released into the body fluid. The released agent is expected to enhace the bone conductivity of the porous titanium.

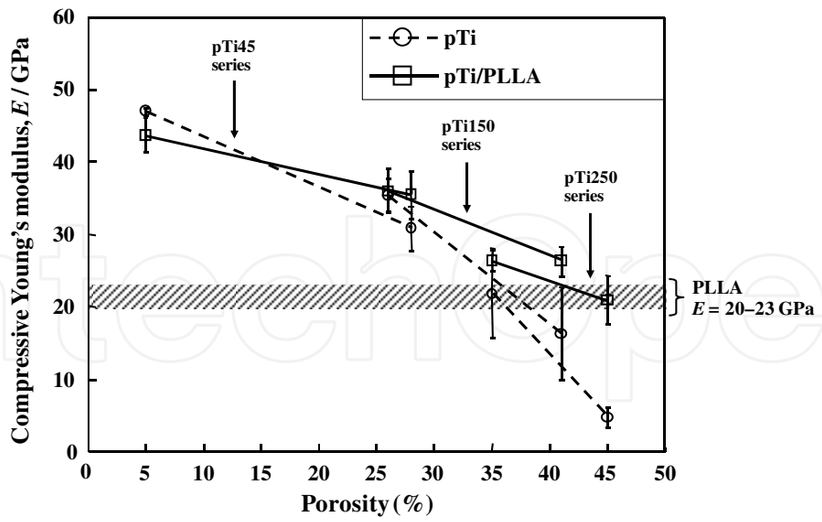


Fig. 8. Compressive Young's moduli of porous titanium (pTi) and porous titanium filled with poly-L-lactic acid (pTi/PLLA).

3.3 Strengthening or increasing endurance while maintaining a low Young's modulus

As already shown in Figs.1 and 2, the tensile strength and 0.2% proof strength of TNTZ both increase with an increase in the cold working ratio, and at high cold working ratio, these parameters become almost equal to those of Ti-6Al-4V ELI (having a tensile strength of around 800 MPa). Good elongation is also achieved when TNTZ is subjected to both cold rolling and cold swaging while the Young's modulus is kept low for both types of treatments.

However, the dynamic strength, i. e., the fatigue strength of TNTZ cannot be improved by severe cold working as shown in Fig. 9 (Akahori, 2003). Therefore, work hardening is not effective for improving the fatigue strength of TNTZ. Precipitation strengthening and dispersion strengthening are expected to improve the fatigue strength of TNTZ.

ω-phase precipitation significantly increases the strength and the Young's modulus of TNTZ as compared to α-phase precipitation, although the ω-phase enhances the brittleness of the alloy. Therefore, a small amount of ω-phase precipitation is expected to improve the fatigue strength of TNTZ while maintaining a low Young's modulus. For this purpose, short-time aging at fairly low temperatures, which enhances the precipitation of small amounts of the ω-phase, is effective.

Figure 10 (Nakai, 2011c) shows the relationship between tensile strength and the Young's modulus of TNTZ subjected to various thermomechanical treatments. In this figure, the terms CR, AT3.6, AT10.8, and AT86.4 indicate TNTZ subjected to severe cold rolling at a reduction ratio of 87 %, and aged at 573 K for 3.6 ks, 10.8 ks, and 86.4 ks, respectively. After severe cold rolling at a reduction ratio of 87 % (the samples are reffered to as (aging treatment) AT samples). The data for TNTZ subjected to aging treatments at 573 K, 598 K, 673 K, and 723 K for various times after solution treatment are also presented. TNTZ aged at 573 K, 673 K, and 723 K for various times after solution treatment showsYoung's moduli greater than or equal to 80 GPa. TNTZ aged at 573 K or 598 K has much higher Young's moduli (around 100-120 GPa). The strengths of these samples are scattered across a larger range than those of TNTZ subjected to aging treatments at other temperatures. These effects

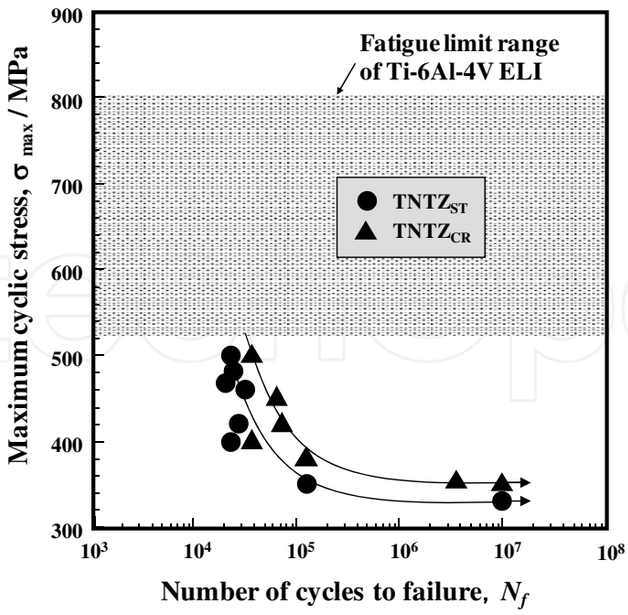


Fig. 9. S-N curves of TNTZ subjected to solution treatment ($TNTZ_{ST}$) and severe cold rolling with a reduction ratio of around 87 % ($TNTZ_{CR}$) along with fatigue limit range of Ti-6Al-4V ELI in air.

are the result of the presence of a large amount of ω-phase; TNTZ containing the ω- phase often exhibits inproved strengths (around 1400 MPa), when the samples do not fail in the elastic deformation range during tensile testing. However, in other cases, the brittleness becomes too high to attain plastic deformation during tensile testing, resulting in relatively low tensile strengths (around 800–900 MPa). In contrast, the TNTZ samples subjected to aging treatment (AT) , except for AT86.4, have Young's moduli below 80 GPa because of the small amount of ω-phase formed as a result of the short aging time. Among the AT samples, AT3.6 and AT10.8 exhibit an excellent balance between high strength and low Young's modulus (numbers 4 and 5 in Fig.10). Therefore, further examination of their fatigue properties was performed.

Figure 11 (Nakai, 2011c) shows the relationship between fatigue strength and Young's modulus of the TNTZ subjected to various thermomechanical treatments. In this figure, the abbreviations of the data are same as used in Fig.10. AT3.6 is classified as being in the low fatigue strength group. The AT10.8 falls in the intermediate level of fatigue strength among the samples, but possesses the highest fatigue strength among the samples having a Young's modulus less than 80 GPa.Therefore, it is possible to effectively control the proper precipitation of the-ω phase, evidenced by the fact that short-time aging at relatively low temperatures improves the fatigue strength of TNTZ while maintaining a low Young's modulus.

The addition of a small amount of ceramics particles such as TiB_2 and Y_2O_3 into the titanium matrix is also expected to improve the fatigue strength of β-type titanium alloys while maintaining a low Young's modulus. Figure 12 (Niinomi, 2011c) shows the Young's modulus and fatigue limit of TNTZ with TiB_2 or Y_2O_3 additions, subjected to severe cold rolling; as a function of B or Y concentration along with those of TNTZ subjected to severe cold rolling ($TNTZ_{CR}$) and solution treatment ($TNTZ_{ST}$), and Ti-6Al-4V ELI (Ti64 ELI). The

fatigue limit of TNTZ is improved with 0.1 mass% and 0.2 mass% B concentration or 0.2 mass% and 0.5 mass% Y concentration while maintaining a very low Young's modulus.

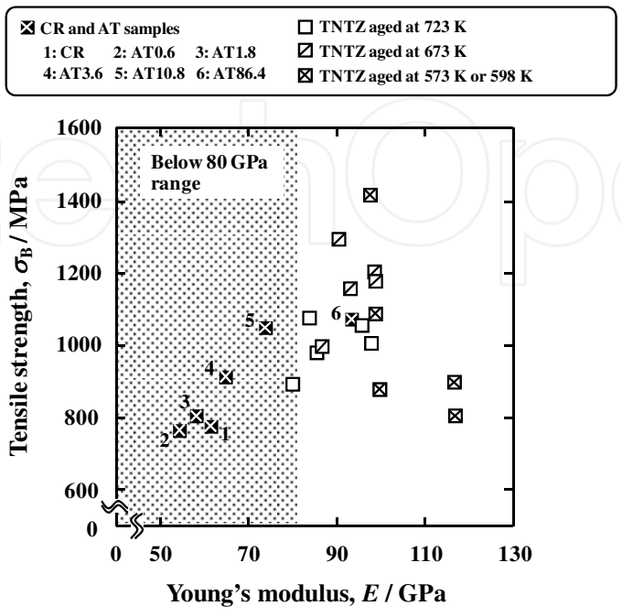


Fig. 10. Relationship between tensile strength and Young's modulus of TNTZ subjected to various thermomechanical treatments.

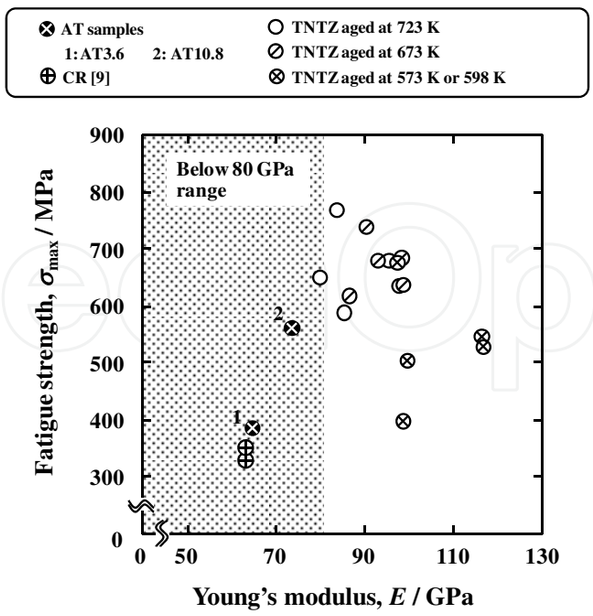


Fig. 11. Relationship between fatigue strength and Young's modulus of TNTZ subjected to various thermomechanical treatments.

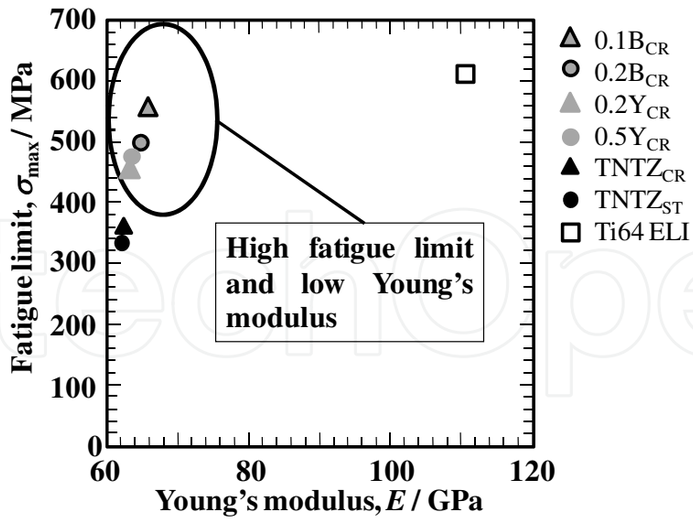


Fig. 12. Relationships between Young's modulus and fatigue limit of TNTZ with B concentrations of 0.1 and 0.2 mass% ($0.1B_{CR}$ and $0.2B_{CR}$,), and Y concentrations of 0.2, 0.5, and 1.0 ($0.2Y_{CR}$, $0.5Y_{CR}$, $1.0Y_{CR}$,) subjected to severe cold rolling, TNTZ subjected to severe cold rolling ($TNTZ_{CR}$), TNTZ subjected to solution treatment ($TNTZ_{ST}$), and Ti-6Al-4V ELI (Ti64 ELI).

4. Bone remodeling and Young's modulus

It is very important to prove that alloys for implants have a Young's modulus similar to that of bone, which will inhibit bone atrophy and induce good bone remodeling as stated above. It is known that the geometry of the implant is another factor used to control the Young's modulus, but the effect of geometry is not treated in this chapter. Studies on bone plates made of low Young's modulus β-type titanium alloy (TNTZ), and conventional and practical (α + β)-type titanium alloy (Ti-6Al-4V ELI), and stainless steel (SUS 316L) in fracture models made into the tibiae of rabbits have been conducted. The Young's moduli of TNTZ, Ti-6Al-4V ELI, and SUS 316L stainless steel used for intramedullary rods, which were measured by three point bending tests, were 58, 108, and 161 GPa, respectively. In that study, an increase in the diameter of the tibia and the double-wall structure in the intramedullary bone tissue were reported to be observed only for the case of the bone plate made of TNTZ as shown in Fig. 13 (Niinomi, 2010a, b). Figure 13 shows that the inner wall bone structure is the original (old) cortical bone whereas the outer wall bone structure is newly formed bone. This is the possible result of bone remodeling with a bone plate having a low Young's modulus.

Furthermore, understanding of the Young's modulus level that is most effective in inhibiting bone atrophy and bone remodeling is necessary. Figure 14 (Niinomi, 2010a) shows the profiles of the extracted bone plates made of TNTZ subjected to solution treatment (TNTZ-ST), TNTZ subjected to aging after solution treatment (TNTZ-AT), and SUS 316 L stainless steel (SUS 316L) attached to the tibiae of the rabbits at 52 weeks after implantation. The Young's moduli of TNTZ-ST, TNTZ-AT, and SUS 316L measured by three-point bending tests were 58 GPa, 78 GPa, and 161 GPa, respectively. The upper surface and sides of each bone plate are covered by newly formed bone, but a fairly large amount of

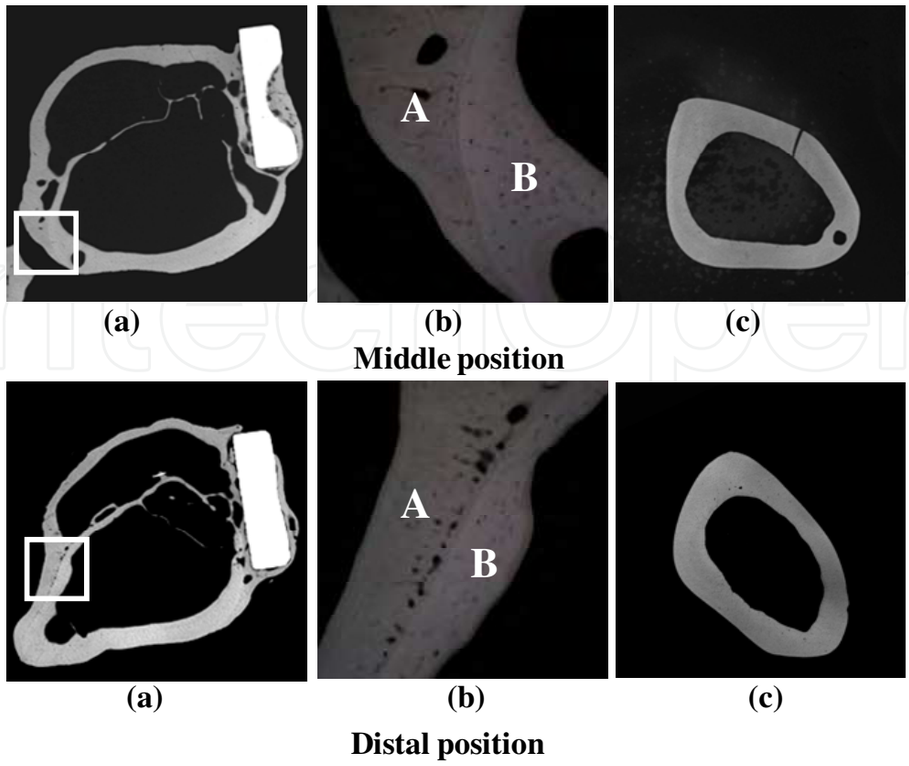


Fig. 13. CMRs of cross sections of fracture models implanted with and without bone plates made of TNTZ at middle position and distal position at 48 weeks after implantation : (a) cross section of fracture model, (b) parts of (a), namely high magnification CMR of branched parts of bones formed outer and inner sides of tibiae, and (c) cross sections of un-implanted tibiae.

newly formed bone can be observed on the heads of the screws made of TNTZ-ST and TNTZ-AT; these have been encircled. Figure 15 (Niinomi, 2010a) shows the optical micrographs of the bone state beneath the bone plates made of TNTZ-ST, TNTZ-AT, and SUS 316L. Bone atrophy can be observed for all the cases, but it is more exident with a titanium having a lower Young's modulus will be advantageous for inhibiting bone atrophy leading to better bone remodeling.



(a) TNTZ-ST **(b) TNTZ-AT** **(c) SUS 3 16L**

Fig. 14. Profiles of extracted bone plates made of (a) TNTZ-ST, (b) TNTZ-AT, and (c) SUS 316L stainless steel fixed to tibiae of rabbits at 52 weeks after implantation.

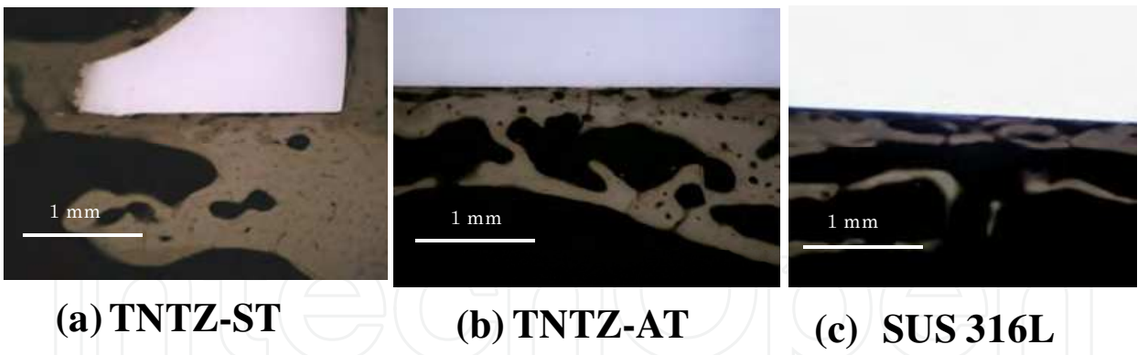


Fig. 15. Optical photographs of bones formed around extracted bone plates made of (a) TNTZ-ST, (b) TNTZ-AT, and (c) SUS 316L stainless steel fixed to tibiae of rabbits at 52 weeks after implantation.

5. Variable Young's modulus titanium alloys

While using low modulus titanium alloys, some surgeons specializing in spinal diseases, such as scoliosis, spondylolisthesis, and spine fracture, pointed out that the amount of spring-back in the implant rods should be small so that the implant offers better handling ability during surgeries. The implant rods undergo bending when they are manually handled by surgeons within the small space inside the patient's body for in-situ spine contouring. It is considered that the amount of spring-back depends on both the strength and the Young's modulus of the implant rod. If two implant rods having the same strength but with different Young's moduli are used, the implant rod having lower Young's modulus shows greater spring-back. Implant rods made of low modulus titanium alloys exhibit a lower Young's modulus, resulting in greater spring back. Thus, a low Young's modulus, which is one of the key features of β-type titanium alloys such as TNTZ as a metallic biomaterial, is obviously a desirable property for patients but becomes an undesirable property for surgeons. Titanium alloys, which satisfy the requirements of both surgeons and patients with regard to the Young's modulus of the implant rod, are currently being developed (Nakai, 2011a).

The amount of spring back is considered to be small for an alloy having a higher Young's modulus than for an alloy having a low Young's modulus. Therefore, a low Young's modulus β-type titanium alloy having a variable Young's modulus that becomes high only at the deformed part may reduce spring-back while simultaneously satisfying the low Young's modulus condition. This concept is called "self-adjustment of Young's modulus". In general, the Young's modulus of metals and alloys does not change upon deformation. However, in the case of certain metastable β-type titanium alloys, non-equilibrium phases such as α′-, α″-, and ω-phases appear in the β matrix during deformation. If the Young's modulus of the deformation-induced phase is higher than that of the original β-phase, the Young's modulus of only the deformed part of the implant rod increases, whereas that of the non-deformed part remains low. In orthopedic operations performed for the treatment of spinal diseases, the implant rod is bent by the surgeons so that it corresponds to the curvature of the spine. Therefore, if a suitable titanium alloy is employed as the implant rod material, spring-back can be suppressed by the deformation-induced phase transformation that occurs during bending in the course of operation, while a low Young's modulus can be retained for patients. In general, the Young's modulus of the ω-phase is much greater than

those of the α-, α′-, α′′-, and β-phase. Among these phases, the ω- , α′-, and α′′-phase can be induced by deformation in β-type titanium alloys with certain chemical compositions.
Ti-12Cr has been reported to be one of the candidate alloys with self-adjustable Young's modulus for biomedical applications. Figure 16 (Nakai, 2011a) shows the Young's moduli of Ti-12Cr subjected to solution treatment (Ti-12Cr-ST) and severe cold rolling (Ti-12Cr-CR) along with those of TNTZ subjected to solution treatment (TNTZ-ST) and severe cold rolling (TNTZ-CR). Ti-12Cr-ST exhibits a low Young's modulus of ~70 GPa; this value is comparable to that of TNTZ-ST, which has been developed as a biomedical β-type titanium alloy having a low Young's modulus. TNTZ-CR also shows a low Young's modulus almost equal to that of TNTZ-ST. Thus, cold rolling leads to negligible change in the Young's modulus of TNTZ. However, in the case of Ti-12Cr, the Young's modulus increases upon cold rolling and that of Ti-12Cr-CR is >80 GPa. The deformation-induced ω phase was detected in Ti-12Cr, but no induced phase was detected in TNTZ. Therefore, the increase in Young's modulus of Ti-12Cr is probably due to the deformation-induced ω phase transformation.

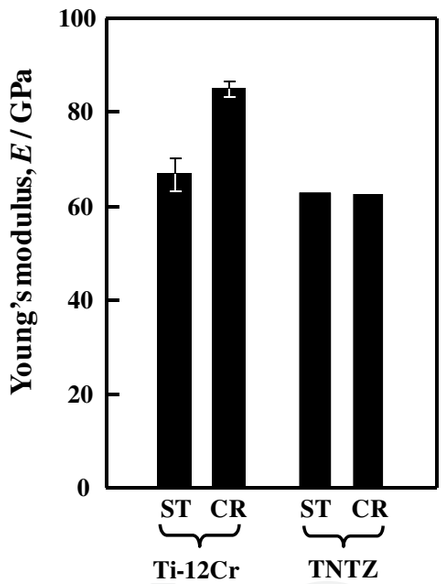


Fig. 16. Comparison of Young's moduli of the designed alloy (Ti-12Cr) and those of an alloy with a low Young's modulus (TNTZ): Ti-12Cr subjected to solution treatment (ST) and cold rolling at a reduction ratio of 10 % (CR), and TNTZ subjected to solution treatment (ST) and severe cold rolling at a reduction ratio of 87 % (CR).

Figure 17 (Nakai, 2011a) shows the tensile properties of Ti-12Cr-ST, Ti-12Cr-CR, TNTZ-ST, and TNTZ-CR. The tensile strengths of both Ti-12Cr-ST and TNTZ-ST show an increase, but the elongation due to cold rolling tends to decrease. This trend is probably caused by the occurrence of work hardening. Furthermore, the tensile strengths of Ti-12Cr-ST and Ti-12Cr-CR may be higher than those of TNTZ-ST and TNTZ-CR, respectively. Moreover, the elongations of Ti-12Cr-ST and Ti-12Cr-CR are >10% and ~10%, respectively. High strength is an essential requirement from the viewpoint of practical application, although such high strength could lead to undesirable spring-back. Therefore, the fundamental composition of Ti-12Cr makes it one of the preferred candidates for use in spinal fixation devices as a biomedical titanium alloy with the ability to self-adjust its Young's modulus.

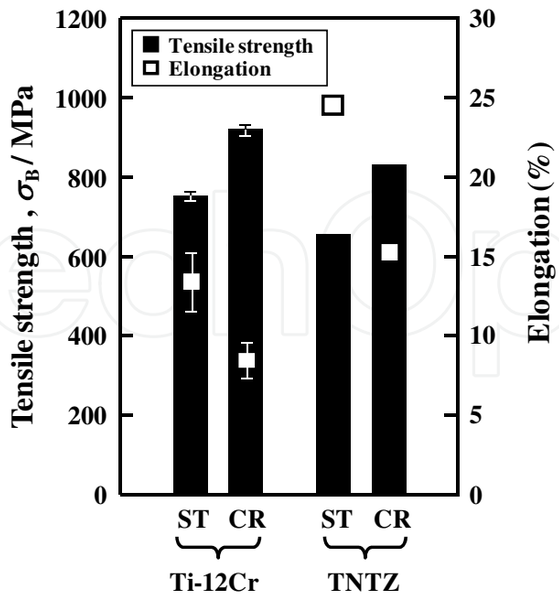


Fig. 17. Comparison of tensile properties of the designed alloy (Ti-12Cr) and those of an alloy with a low Young's modulus (TNTZ): Ti-12Cr subjected to solution treatment (ST) and cold rolling at a reduction ratio of 10 % (CR), and TNTZ subjected to solution treatment (ST) and severe cold rolling at a reduction ratio of 87 % (CR).

6. Low Young's modulus titanium alloys for reconstructive implant devices

In the case of some types of internal fixation devices implanted into the bone marrow such as femoral, tibia, and humeral marrow, in the case of screws used for bone plate fixation (Kobayashi, 2007), and in the case of implants used for children, which otherwise would grow into the bone, it is essential to remove the internal fixation device after surgery owing to certain specific indications; these indications include significant local symptoms such as palpable hardware, wound dehiscence/exposure of hardware, or athletes returning to contact sport (Kambouroglou, 1998) (Coook, 1985). The assimilation of removable internal fixation devices into the bone due to precipitation of calcium phosphate might cause refracture of the bone during the removal of the fixation device. Therefore, in these cases, it is essential to prevent the adhesion of the alloys with the bone tissues. Hence, considering this requirement, it is essential to inhibit the precipitation of calcium phosphate. It is reported that Zr, which is a non-toxic and allergy-free element, has the ability to prevent precipitation of calcium phosphate (Kawahara, 1963), and Ti alloys with Zr contents exceeding 25 mass% prevent the formation of calcium phosphate, which is the main component of human bones (Narushima, 2005). Thus, Ti-30Zr-Mo has been proposed as a low Young's modulus titanium based biomaterial for use in removable implants.

Figure 18 (Zhao, 2011) shows the Young's moduli of Ti-30Zr-xMo (x = 5, 6, and 7) subjected to solution treatment and those of the alloys considered for comparison. The Young's modulus of Ti-30Zr-xMo is lower than that of the alloys considered for comparison except TNTZ. The minimumYoung's modulus is obtained for Ti-30Zr-6Mo with a value of around 60 GPa, and TNTZ also shows a low Young's modulus.

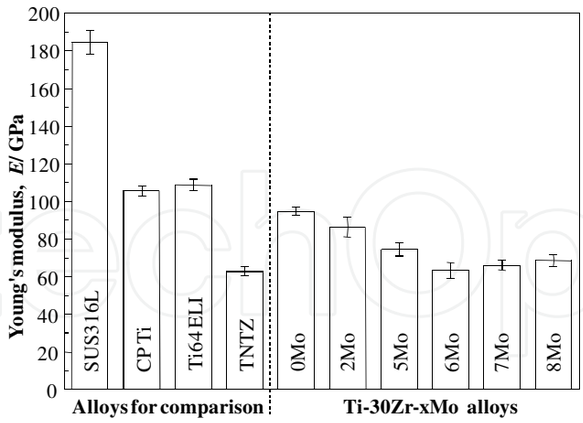


Fig. 18. Young's moduli of Ti-30Zr-*x*Mo (*x* = 0, 2, 5, 6, 7, and 8 mass%) alloys subjected to solution treatment and the alloys considered for comparison.

In orthopedic applications, ideal biomedical implant materials are required to have high strength and a low Young's modulus. The elastic admissible strain, defined as the strength-to-modulus ratio, is a useful parameter considered in orthopedic applications. The higher the elastic admissible strain, the more suitable are the materials for such applications (Williams , 1971). Figure 19 (zhao, 2011) shows the distribution of the as-solutionized Ti-30Zr-xMo and the alloys considered for comparison in the plot of elastic admissible strain against elongation. Ti-30Zr-6Mo and -7Mo exhibit larger elongation and higher elastic admissible strain than the other Ti-30Zr-xMo and SUS316L, CP Ti, Ti64 ELI, and TNTZ.

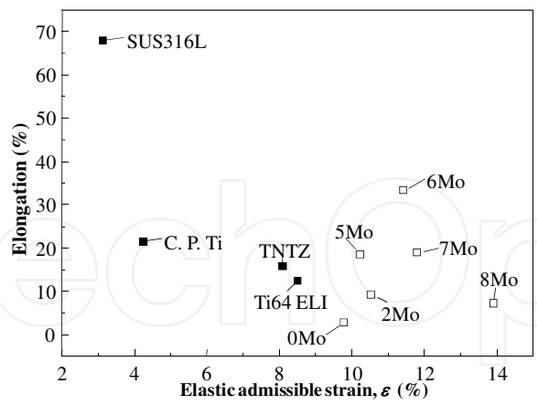


Fig. 19. Distribution of solutionized Ti-30Zr-*x*Mo (*x* = 0, 2, 5, 6, 7, and 8 mass%) alloys and the alloys (SUS 316 L stainless steel, TNTZ and commercially pure titanium (C.P.Ti) considered for comparison in a plot of elastic admissible strain against elongation.

Figure 20 (Zhao, 2011) shows the density of cells cultured for 24 h in the presence of Ti-30Zr-7Mo and the alloys considered for comparison. Ti-30Zr-7Mo has the highest value of cell density. Therefore, Ti-30Zr-6Mo and Ti-30Zr-7Mo show promising potential to be new candidates for use in biomedical applications.

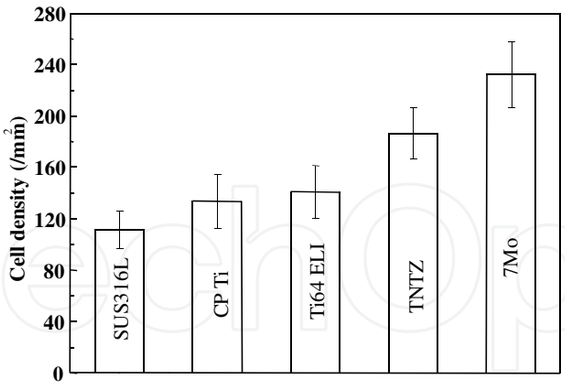


Fig. 20. Density of cells cultured in 7Mo and the alloys (SUS 316 L stainless steel, commercially pure titanium (CPTi), Ti-6Al-4V ELI (Ti64ELI), and TNTZ) considered for comparison.

Figure 21 (Zhao, 2011) shows Young's moduli of Ti-30Zr-5Mo, Ti-30Zr--6Mo, and Ti-30Zr--7Mo subjected to solution treatment (referred to as 5Mo-ST, 6Mo-ST, and 7Mo-ST, respectively) and subjected to cold rolling at a reduction ratio of 10 % (referred to as 5Mo-CR, 6Mo-CR, and 7Mo-CR respectively). In the ST samples, with increasing Mo content, the Young's modulus initially decreases from 75 GPa in 5Mo-ST to 63 GPa in 6Mo-ST and then increases slightly to 66 GPa in 7Mo-ST. The Young's moduli of the ST alloys are lower than those of conventional biomedical alloys such as SUS316L stainless steel (SUS 316L), commercial pure Ti (CP Ti), and Ti–6Al–4V extra-low interstitial alloy (Ti64 ELI). The change in Young's modulus after cold rolling varies with the Mo content: the Young's modulus of 5Mo-CR decreases drastically to 59 GPa from 75 GPa (after ST), and the Young's modulus of 6Mo-CR deceases to 61 GPa from 63 GPa (after ST). However, the Young's modulus of 7Mo-CR increases to 73 GPa from 66 GPa (after ST). Therefore, Ti-30Zr-7Mo is expected to be a Young's modulus self-adjustable titanium alloy for biomedical applications.

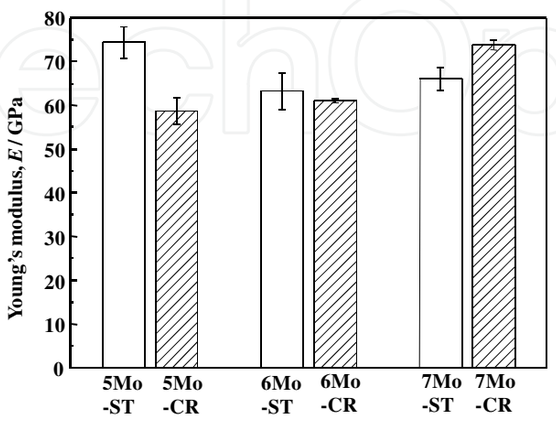


Fig. 21. Young's moduli of Ti–30Zr–(5, 6, 7)Mo alloys subjected to solution treatment (5Mo-, 6Mo-, 7Mo-ST) and cold-rolling (6Mo-, 6Mo-, 7Mo-CR).

7. Summary

The removal of metallic biomaterials from implanted bone tissue is fairly new concept because tight adhesion between the metallic biomaterial and bone is currently one of the targets of biomaterials researchers.

Nowadays, conflicting properties of a low Young's modulus to inhibit bone atrophy and high Young's modulus to inhibit spring-back are simultaneously desired in biomaterials. i.e., Young's modulus self-adjustment ability is required in the metallic biomaterials. In order to satisfy these demands, metastable β-type titanium alloys that exhibit deformation-induced transformation are prospective candidates materials can be selectively changed from low to high at the deformation point. However, the degree of the change in the Young's modulus is currently insufficient to satisfy the biomaterial demand and thus, further investigation of these kinds of titanium alloys is warranted.

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These contribution books collect reviews and original articles from eminent experts working in the interdisciplinary arena of biomaterial development and use. From their direct and recent experience, the readers can achieve a wide vision on the new and ongoing potentials of different synthetic and engineered biomaterials. Contributions were not selected based on a direct market or clinical interest, than on results coming from very fundamental studies which have been mainly gathered for this book. This fact will also allow to gain a more general view of what and how the various biomaterials can do and work for, along with the methodologies necessary to design, develop and characterize them, without the restrictions necessarily imposed by industrial or profit concerns. The book collects 22 chapters related to recent researches on new materials, particularly dealing with their potential and different applications in biomedicine and clinics: from tissue engineering to polymeric scaffolds, from bone mimetic products to prostheses, up to strategies to manage their interaction with living cells.

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