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Surface Treatments of Nearly Equiatomic NiTi Alloy (Nitinol) for Surgical Implants

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1. Introduction

Since the discovery of the shape memory effect in equiatomic NiTi alloy by Buechler in 1962 in the Naval Ordnance Laboratory [1], nitinol (Nickel-Titanium Naval Ordnance Laboratory) has attracted a great deal of commercial interest especially in medical applications [2, 3]. T. Duerig, A. Pelton, and D. Stockel wrote an excellence overview on nitinol medical applications in 1999 [3]. They pointed out that there were three reasons for the sudden explosive growth of Nitinol in the 1990's. The most important was that the medical industry had been trying to pare costs and simplify medical procedures. Conventional materials like 316L stainless steel could not fulfill this new demand by medical devices. Furthermore, the availability of microtubing and ability to laser cut tubings with high precision favored new materials like Nitinol. Last but not least, sharing of technology developed by materials scientists and companies among product designers and doctors should not be underestimated. They specifically pointed out 11 specific reasons for the application of Nitinol to the medical industry [3, 4]:

- a. elastic deployment allowing an efficient deployment of a medical device;
- b. thermal deployment and by using the shape memory effect, the nitinol device can recover to its 'pre-programmed' shape by body temperature after the deployment;
- c. kink resistance which allow the medical device to pass through tortuous paths without stain localization and changing its shape;
- d. good biocompatibility which means that the foreign implants are well accepted by the body. Nitinol has been reported to have extremely good biocompatibility due to the formation of a passive titanium-oxide layer (TiO₂) [3]. However, Ni is allergenic and toxic to humans and reports have shown that the Ni release from commercial ready-to-use nitinol orthodontic wires vary in a wide range from 0.2 to 7 $\mu\text{g cm}^{-2}$ [5]. Therefore, Ni release from nitinol remains a serious health concern and surface modification of nitinol devices will be discussed later in this chapter;
- e. constant stress allowing the design of a medical device that applies a constant stress over a wide range of shapes;

- f. biomechanical compatibility meaning that a medical implant that is mechanically similar to the adjacent biological materials promotes bone in-growth and proper healing by sharing loads with the surrounding tissue;
- g. dynamic interference implying that the long-range nature of nitinol causes less damage to the surrounding tissue;
- h. hysteresis which is a desirable feature for stents that provide a very low dynamic outward force (COF) and a very high radial resistive force (RRF);
- i. magnetic resonance image (MRI) compatibility because nitinol is non-ferromagnetic that allows a clearer and crisper magnetic resonance image than stainless steel;
- j. exceptional fatigue resistance under high strain making nitinol drills perfect in dental root canal procedures;
- k. uniform plastic deformation having advantages in balloon expansion nitinol stents.

2. Shape memory effect and super-elasticity

Nitinol shape memory alloys (SMA's) have been used in biomedical implants for more than three decades because they can recover from large strain through the application of heat [6, 7]. Nitinol shape memory alloys undergo thermoelastic martensitic transformation giving rise to the shape memory effect (SME) and superelasticity (SE) also named as pseudoelasticity (PE) properties. Since the body temperature is a very stable, the phase transition temperature can be precisely control in order to maximize the SME and SE behavior at 37°C. The SME and SE properties are related to the thermo-elastic martensitic transformation and reverse phase transformation. Some phase transformation is irreversible and this irreversible process repeats during thermal cycles. Heat treatment of nitinol focuses on the austenitic phase transition (reverse martensitic transformation). SE depends on the temperature difference ΔT between the working temperature T and austenite finish temperature A_f . The forward and reverse phase transition temperatures of nitinol between the martensitic phase (B19') and austenitic phase (B2) must be carefully determined during the heat treatment process. The important heat treatment parameters include the cooling rate, heat treatment temperature, and processing time. The heat treatment temperature can be divided into three ranges, solid solution between 800 and 900 °C, aging between 400 and 550°C, and another aging treatment between 200 and 400 °C. Cooling can be preformed in different ways, for example, furnace cooling, air cooling, water quenching, etc. To achieve a phase transition temperature at 37°C, the nitinol devices can be, for example, heat-treated at 500°C for 1 hr in a furnace followed by water quenching [8] or heat-treated at 580°C for 30 mins in air followed by quenching in air to room temperature [9]. It is worth mentioning that any surface modification method should not vary the phase transition temperature and shall be performed at a relatively low temperature. Previous studies have shown that a treatment temperature of 210°C for 4 hours can destroy the super-elastic and shape memory effects at body temperature and must be avoid [8]. We will discuss the importance of maintaining a low treatment temperature for surface modification of nitinol in the following sections.

3. Ntinol medical implants and devices

Stainless steel has been replaced by nitinol in many traditional medical implants. Because of the super-elasticity and shape memory effect, nitinol has been used to make many novel

devices and several successful and representative nitinol implants and devices are described below.

1. Stents

Although the word “stents” was originally used in dentistry, it is nowadays reserved for devices used to scaffold the inside circumference of tubular passages or lumens, i.e., the biliary duct, esophagus, and blood vessels including coronary, carotid, iliac, aorta, and femoral arteries [3, 4]. Stenting is a typical procedure following balloon angioplasty. The application of a stent immediately after angioplasty shows a significant decrease of propensity for restenosis. Nitinol is preferred in stents because of its outstanding super-elasticity. It is 10 to 20 times more flexible than stainless steel, and it can spring back with strain as high as 11%. Figure 1 depicts a crush recoverable nitinol stent [4]. Vessels such as the carotid and femoral arteries are always subjected to outside pressure which may crush stainless steel stents leading to serious consequences. Nitinol urethral stents also exhibit excellent biocompatibility with no evidence of foreign body reactions or corrosion when tested in dogs [10].

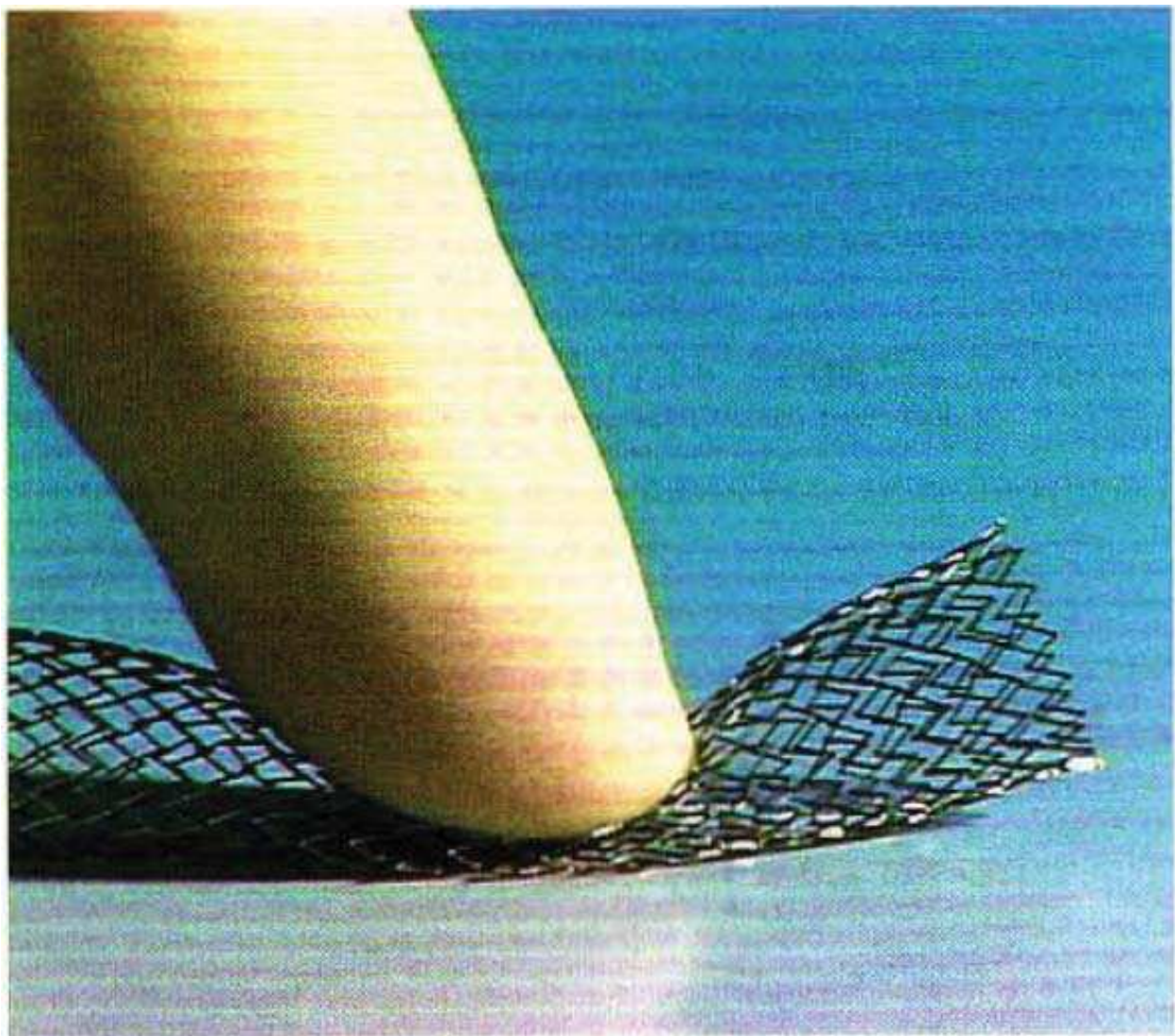


Fig. 1. Crush recoverable nitinol stent (Reproduced from ref [4]).

2. Clamps for small bone surgery

A good example of medical applications of nitinol is clamps used in small bone surgery [11]. The provision of stable fixation of bone fragments is essential to small bone surgery because passive and active motion can start soon thereafter [11]. Moreover, early rehabilitation can prevent rigidity of the broken joints and expedite healing [11]. The key advantage of using shape memory alloy is that the fixative can contract by applying heat stimulus after the surgery. This contraction does not only reduce or eliminate the gap between the bone fragments to be joined, but also applies the appropriate compression, consequently resulting in stable fixation and promoting healing. Figure 2 depicts a successful talocalcaneal arthrodesis by using three TiNi clamps [11]. However, sterilization must be done at a temperature below 45°C at which phase transformation occurs. Gamma irradiation is used for sterilization of nitinol clamps.

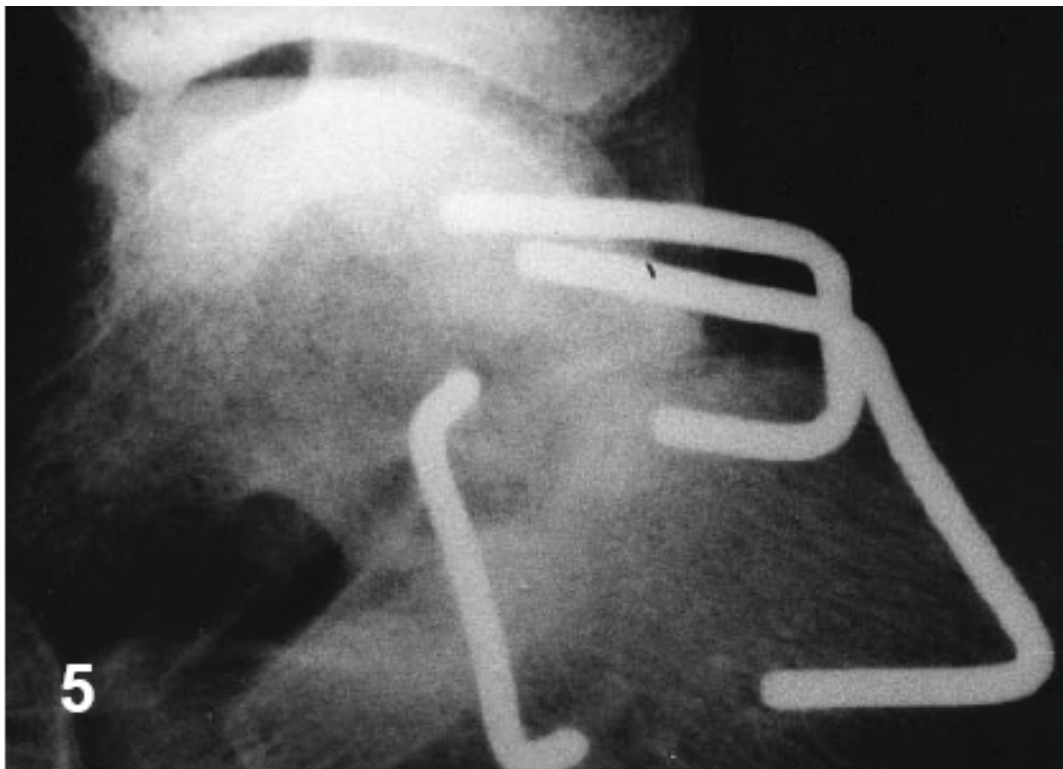


Fig. 2. Talocalcaneal arthrodesis by using three nitinol clamps (Reproduced from ref [11]).

3. S-shape bar for surgical correction of scoliosis

The shape memory effect of nitinol, that is, being flexible at low temperature but retaining its original shape when heated, has attracted a lot of interest for scoliosis correction [12, 13]. In cases of severe spinal deformity, surgeries have to be performed to straighten the patient's spine. The success of correction depends on how well the fixative, i.e., the S-shape rod, is fixed to the spine. Moreover, a force that is too large can cause bone fracture and tissue damage. On the other hand, a force being too small will lead to under-correction. Owing to the super-elastic and shape memory properties, nitinol is the ideal materials choice for the S-shape fixing rod. Figure 3 demonstrates the constant recovery force of the rod after implantation into a goat verifying the feasibility of the surgical procedures [13]. Before the operation, the rod is coiled down to below the phase transition temperature, for example 15°C which is lower than the body temperature. At this temperature, the rod is soft

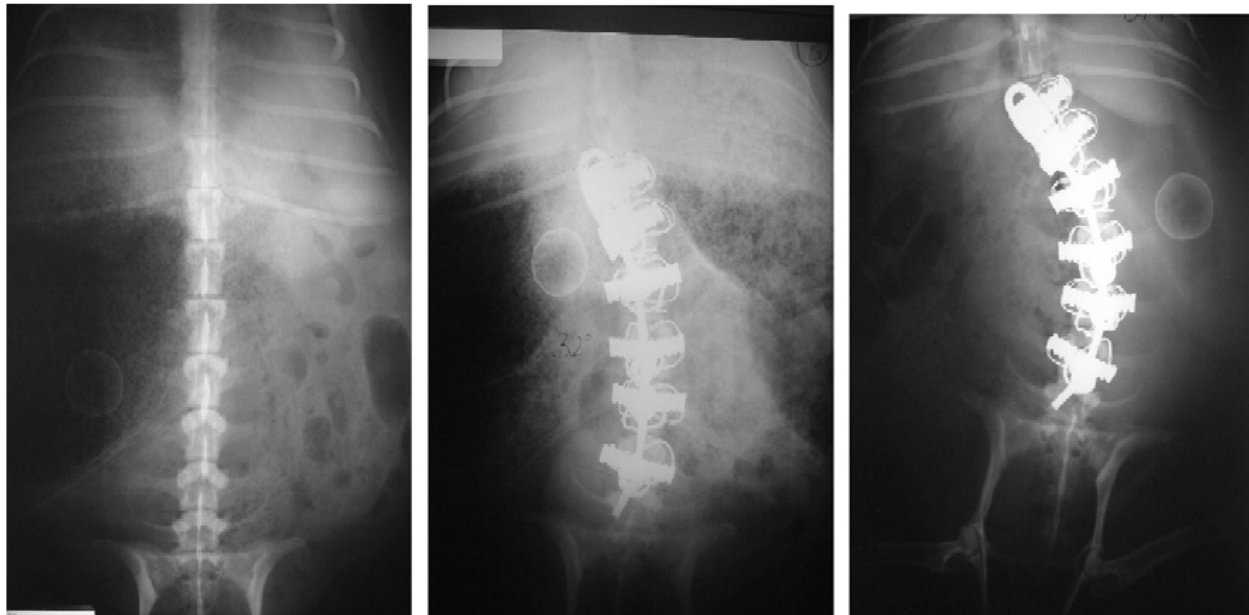


Fig. 3. X-ray photos of the spine of the operated goat: (Left) before surgery; (Middle) one day after implantation of a nitinol rod; (Right) one week after surgery. The spine of the goat that was straight before surgery became progressively bent by the constant recovery force of the rod thereby verifying the feasibility of the surgical procedures (Reproduced from [13]).

and can be bent to fit the deformed spinal. After the operation, the nitinol rod is heated to the body temperature of 37°C to revert back to its original shape. Therefore, gradual correction can take place under a constant force obviating the need for multiple corrective surgeries.

4. Patellar concentrator

The nitinol patellar concentrator (NT-PC) is designed for initial and continuous compression of patellar fractures [14]. NT-PC consists of two basis patellae claws, three apex patella claws, and a conjunctive waist [14]. The NT-PC is constructed by nitinol plates of different sizes that have undergone different heat treatments. The final product exhibits the one-way shape memory effect at a phase transformation temperature of $30 \pm 2^{\circ}\text{C}$ and reversible deformation of 8%. During implantation, the NT-PC is cooled down to below 30°C and unfolded in aqua astricta. The patellar concentrator can easily be put on to the fractured patellar. Figure 4 displays a nitinol patellar concentrator downloaded from Yangzhou Yahua Biological Technics Project Co. Ltd. After the operation, the concentrator is warmed and recovers to its original shape with a compressive force. This compressive force will fix the concentrator tightly onto the patellar until the fracture heals. The key element of treating patellar fractures is to reduce facies articularis and it is known that the memorial compressive stress generated by the nitinol patellar concentrator can promote the healing of cartilage.

4. Problematic leaching of Ni

Although unique properties such as the shape memory effect and super-elasticity can enhance the performance of medical implants, the biocompatibility of the materials remains a concern [15]. There are two main factors determining the biocompatibility of materials, namely the host reaction induced by the materials and degradation of the materials in the body environment. Nitinol consists of 50% of Ni and dissolution of Ni ions can induce



Fig. 4. Nitinol patellar concentrator downloaded from Yangzhou Yahua Biological Technics Project Co. Ltd.

allergic [16], toxic [17], and carcinogenic [18] effects. The corrosion performance of nitinol *in vivo* determines the release of Ni ions. Studies have shown that the corrosion performance can range from excellent to poor indicating the lack of complete understanding of the chemistry of the nitinol surface [15]. For small diameter devices such as fine wires and caliber vascular stents, a small surface defect may be sufficient to increase the leaching of Ni. Implants in the body are usually under stress / strain because of loading / unloading conditions and such actions can aggravate Ni release. In addition, sterilization procedures may modify the materials surface and accelerate Ni release and a multitude of factors must be considered simultaneously.

In vivo studies of nitinol clamps show that after proper passivation, a 3-4 nm thick TiO_2 layer forms. Afterwards, only traces of metallic Ni are detected and no major change is observed during a period between 4 and 12 months after implantation [19]. In the investigation, the proper passivation procedure calls for the samples (clamps with desired structure and memory parameters) to be etched in a solution of HF, HNO_3 and H_2O (1:2:3 vol% for 30mins), pre-deformed, ultrasonically cleaned in ethanol, and sterilized by X-ray at room temperature [19]. However, after improper surface passivation by sputter cleaning and re-oxidation in pure oxygen (5 Torr, room temperature, 10 mins), trace amounts of ~1 at% of Ni are detected [19]. Although oxidation can promote the growth of a passive native film, it is usually not complete at room temperature [15]. At high temperature, a heterogeneous surface with a mixture of various types of oxide tends to form and a mixture of various phases rather than a single oxide renders nitinol more vulnerable to corrosion.

Shabalovskaya et al. reviewed critically the nitinol surfaces and surface modification for medical applications [5]. Electrolytic etching can induce highly porous NiTi surfaces that

may increase Ni release, but this porous structure can also promote cell attachment [20]. After chemical etching and electropolishing, the surface oxide films are a few nanometers thick. Oxidation is promoted by boiling in water thereafter. The gentle treatment of boiling in water assists atomic diffusion and Ni release into the water and the oxide thickness increases to 10 to 20 nm. This oxide layer which is more stoichiometric depletes surface Ni and mitigates subsequent Ni release. It has been reported that anodization of nitinol does not reduce the Ni surface content and a severely cracked surface is obtained using the optimized anodizing parameters. However, it is not surprising that good corrosion resistance is observed after anodization and chemical etching following by boiling in water. No surface cracking upon 6% strain is observed after immersion in a corrosive solution.

Prevention of Ni release can be done by surface oxidation via heat treatment in air, argon and partially reduced atmosphere [5]. After oxidation in air at between 300 and 500°C for 30 mins, TiO, pure Ni, and NiTi B2 are detected. When the annealing temperature goes up to 600 °C, different phases of TiO₂, Ni, and Ni₃Ti are observed. However, the simultaneously presence of austenitic B₂ and martensitic NiTi phases implies alteration in the shape recovery temperature. Annealing at 600°C can produce a Ti oxide film at least 5 times thicker but accumulate Ni below the surface. The accumulated Ni can be eliminated by chemical etching. Since the shape memory and super-elasticity of nitinol is optimized in the temperature ranges of 450 to 550°C, the oxidation temperature should be below 300°C.

Laser surface melting (LSM) can be carried out in either argon or air (dry) [21]. New phases of Ti₂Ni and TiNi₃ are observed and part of the surface changes to martensite B19' in argon. When LSM is conducted on nitinol in dry air, TiO₂ and Ti₄Ni₄O phases are observed from the near surface. Ni release is significantly reduced only on the first day of exposure to Hanks' solution. However, the presence of the B19' martensite phase after LSM is an indication that the surface has been overheated.

Diamond-like carbon (DLC) is well known for its good mechanical properties such as high hardness, low friction coefficient, chemical inertness, high corrosion resistance, and excellent biocompatibility [5, 22]. DLC can be deposited on NiTi devices to prevent Ni release and improve the biocompatibility. Different gases (acetylene C₂H₂ and benzene C₆H₆) and processes such as no-bias deposition and plasma immersion ion implantation have been adopted to synthesize DLC on NiTi. In plasma immersion ion implantation (PIII), the sample is immersed in a gas plasma and then pulse-biased to a high negative voltage of tens of kV [13]. A plasma sheath forms around the sample when the voltage pulse is applied. Positive ions are accelerated by the electric field and simultaneously bombard all exposed surfaces on the sample. Therefore, PIII is a non-line-of-sight process especially suitable for medical implants with a complex geometry [13]. However, direct coating results in delamination of the deposited layers and SiC is used as an interlayer to improve adhesion. A 50 nm thick DLC coating with enhanced hardness and Young's modulus can be obtained by annealing at 600°C for 5 hrs after PIII but it should be noted that annealing at 600°C for 5 h may alter the shape memory properties and super-elasticity.

5. TiN layer to blocking Ni release from Nitinol

Titanium nitride belongs to the refractory transition metal family [23] and consists of both covalent and metallic bonds [23, 24]. TiN has found many applications in microelectronic fabrication because of its good conductivity and excellent adhesion. It is used as a diffusion barrier between the silicon substrate and aluminum metallization. TiN is also commonly

used in coating cutting tools because of its high hardness and good resistance to wear and corrosion. TiN is useful in biomedical applications because of its intrinsic biocompatibility and can be found on orthopedic implants such as hip. The materials are also widely used as hard coatings on dental implants and dental surgical tools. Direct implantation of nitrogen can produce titanium nitride is possible because TiN forms preferentially over NiN.

The powder immersion reaction assisted coating (PIRAC) nitriding method has been developed to produce TiN on NiTi [24]. NiTi samples with a phase transform temperature at $A_f = 15^\circ\text{C}$ are annealing at 900°C for 1.5 h and then 1000°C for 1 hr in sealed containers. Nitrogen atoms diffuse into the samples and atmospheric oxygen is stopped by a steel foil with a large percentage of Cr. The modified surface consists of a thin outer layer of TiN and a thicker Ti_2Ni layer underneath. The PIRAC samples exhibit significantly improved corrosion resistance. No pitting is observed on the surface and the surface hardness is also increased remarkably. Hence, leaching of harmful Ni *in vivo* can be reduced. However, a fully crystallized TiN layer may not sustain deformation without cracking and annealing at 900°C for 1.5 hrs will no doubt alter the phase transformation temperature.

Laser gas nitriding (LGN) has been demonstrated to improve the surface performance of Ti and Ti alloys [25]. LGN is conducted on NiTi with a laser beam emitted from a 2 kW Nd-YAG laser at a wavelength of $1.06\ \mu\text{m}$ [25]. At a scanning rate of 5 mm/sec with a beam diameter of 2 mm, defect free single tracks are observed on the NiTi shape memory alloy plates. By overlapping the single track at the 50% melt width interval, a large nitrided surface is achieved [25]. The defect/crack free TiN layer protects the NiTi surface from wear and corrosion and therefore reduces leaching of harmful Ni. However, LGN is a line-of-sight process and may not handle NiTi biomedical devices with a complex shape. Moreover, the strong laser may affect the phase transformation temperature especially for very thin NiTi samples such as RITA tissue ablation devices with sharp and curved tubular needles [3].

Plasma immersion ion implantation (PIII) is well known for the production of dense, crack free surface layers [26]. It is a non-line-of-sight process and can implant the whole surface of a sample with an odd shape. It also boast a high throughput [13, 26, 27]. Nitrogen PIII has been conducted on NiTi alloy to produce TiN on the surface [8, 28, 29]. After nitrogen PIII, the Ni concentration in the implanted surface is much lower than that in the unimplanted surfaces [29]. A high degree of cell proliferation after 8 days of culturing is observed on the N-PIII samples as well [29]. The depression of near-surface Ni and good biocompatibility can be attributed to the formation of the TiN barrier layer [26, 29]. However, the phase transformation temperature and hence the shape memory effect and super-elasticity properties of the the NiTi alloy strongly depend on the ion energy and treatment temperature [8, 28]. The sample temperature during the PIII treatment has been observed to be over 210°C [8] and at this temperature, the preset shape memory effect and super-elasticity, i.e., the phase transformation temperature, can be modified and even lost [8]. Therefore, the treatment parameters such as pulsing frequency, total treatment time, and other factors must be carefully optimized [8, 28].

6. Advantages of formation TiN layer on Nitinol implants by Quasi-DC PIII

As described in previous sections, a titanium nitride barrier is a good choice to mitigate Ni release and TiN also increases the hardness, wear resistance, and biocompatibility. However, almost all the available methods used to produce titanium nitride involve the use

of direct or indirect high temperature annealing which can shift the phase transformation temperature and destroy the preset shape memory function at the body temperature. One can suggest that surface modification can be performed before the phase temperature setting procedure, but it is not very practical. To fine tune the phase transformation temperature requires precise thermal cycling and the surface modification process may not fit well. The most important reason is that the manufacturers seldom vary their production line to accommodate other process and any additional processes are regarded to increase production steps and cost.

The quality of the titanium nitride film formed on NiTi implants may differ from those on conventional products such as cutting tools. The TiN coatings on these products tend to be quite thick (on the order of μm or more) and hard (harder than stainless steel) because good wear resistance is required. Therefore, a fully crystalline TiN layer is preferred. However, the requirements for biomedical implants are quite different. In the human body, the NiTi devices are surrounded by mainly soft tissues and so an extremely hard surface is not necessary since it may damage the surrounding tissues. It has been shown that a uniform amorphous titanium oxide layer can withstand corrosion much better than a non-uniform titanium oxide layer composed of various phases and many cracks. Unlike cutting tools which are hard, NiTi implants are super-elastic that can withstand many cycles of stress and strain loadings. A thick and fully crystallized TiN layer has a better chance to crack during the stress and strain cycles. Therefore, a uniform amorphous titanium nitride layer of several tens of nm thick is sufficient to block harmful Ni release from NiTi implants.

Our recently developed quasi direct-current (DC) plasma immersion ion implantation that can process three dimensional (3D) objects has large potential in the surface modification of NiTi biomedical devices [30]. In conventional PIII, a negative high voltage between 20 and 40 kV or higher and with a frequency between 50Hz and 200 Hz is applied to the sample. The pulse duration is typically between 30 and 100 μsec . Even for a short pulse width of 30 μsec , the ion sheath can propagate far away from the sample at a negative voltage of -35kV. The implantation process becomes nonuniform spatially especially on 3D objects since the ion sheath is not conformal to the objects. To improve the uniformity of the PIII treatment, we can reduce the pulse duration and increase the ion (plasma) density. However, increasing the ion density will increase the conductivity in space and may cause arcing problems especially when the objects have sharp edges and corners. Using a smaller voltage may alleviate the arcing problems but the surface modified layer will be thinner. To compensate for the reduced efficiency when adopting a short pulse duration, the pulsing frequency and treatment time need to be increases. A high pulsing frequency will increase the workload of the power supply and pulse modulator. The displacement current generated (displacement current is a quantity that is defined in terms of the rate of change of electric displacement field) during the pulse rise time will increase with high pulsing frequency. Therefore, the sample temperature during PIII treatment is inevitably increased and the mechanical properties of the NiTi sample can be compromised.

In the quasi DC-PIII setup, the reliability and stability of the implantation process is improved by using a grounded Al housing and stainless steel mesh surrounding the specimen [30]. Numerical simulation reveals that the implantation fluence distribution along the major curvature of an S-shape bar used in surgical correction of scoliosis is more uniform and less than that obtained by conventional PIII [31]. X-ray photoelectron spectroscopy (XPS) depth profiling reveals that the retained dose uniformity along the length of the S-shape bar is greatly improved and differential scanning calorimetry (DSC)

curves also illustrate that the sample temperature during implantation is well controlled and does not affect the shape memory effect and other mechanical properties of the NiTi alloy [32].

The quasi DC PIII setup for 3D objects is based on an extension of the direct-current PIII idea developed in the Plasma Laboratory of City University of Hong Kong in 2000 originally used for large planar samples such as silicon wafers [33]. To reduce the unnecessary ion currents impacting the sample stage, the stage is enshrouded by a grounded metal cylindrical cage [30]. To further minimize the non-uniformity ion fluence caused by the non-conformal expanding ion sheath, the S-shape bar is surrounded by a cylindrical stainless mesh cage. To completely shield off the negative high voltage, a flat solid steel dish is placed on top of the mesh cage. The schematic of the 3D setup is displayed Figure 5 [30]. Numerical simulation discloses that the expanding ion sheath is blocked by the grounded mesh cage. Although the ion sheath covers up more ions through expansion, ions can diffuse inside the mesh cage since a weak RF sheath is established between the bulk plasma and grounded mesh cage [34]. Compared to conventional PIII, the total ion flux implanted into the S-shape bar is reduced. By using a grounded mesh cage, the plasma density can be lower and therefore, arcing problems can be alleviated in spite of the use of a high negative voltage. A longer pulse duration can also be employed and the displacement currents generated during the pulse rise-time can be reduced as well. In addition, the sample temperature can be more precisely controlled and the implanted dose uniformity can be improved by rotating the samples [32]. We have recently applied nitrogen quasi DC PIII to patellar concentrator and other bones concentrator. A uniform gold color is observed from the samples shown in Fig. 6 suggesting that a relatively uniform titanium nitride layer is formed on the entire surface of the sample. This method has many applications and more work is being done in our laboratory in order to realize its full potential.

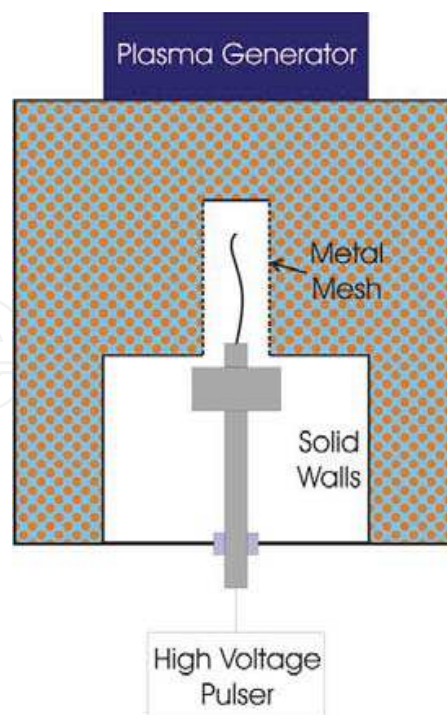


Fig. 5. Quasi-DC PIII setup with grounded stainless steel cage encompassing the sample and grounded Al (Reproduced from [30]).



Fig. 6. Patellar concentrators and other bone concentrators with the left one showing two raw concentrators and the right one showing the three concentrators after the quasi DC-PIII treatment.

7. Conclusion

This chapter briefly reviews the mechanical properties of NiTi shape memory alloys and applications in biomedical engineering. Because of leaching of harmful Ni from the materials to biological issues, various methods have been adopted. Some of the important surface methods are described and particular emphasis is put on the novel direct-current plasma immersion ion implantation technique which has high potential.

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