Review

Jianing Zhu, Qunfeng Zeng* and Tao Fu

An updated review on TiNi alloy for biomedical applications

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Abstract: This manuscript has provided an overview of the development of TiNi alloys and their applications in biomedicine. The microstructures and properties of TiNi alloys are first introduced. The breakthroughs in the manufacturing and applications in biomedicine of TiNi alloys in recent years have been achieved by scientists and are presented in the present paper. It is well known that the properties of TiNi alloys are affected by the modification methods on the surface of bulk TiNi alloys. The main preparation technologies of TiNi alloy coatings are evaluated, with particular attention to several spray technologies. Then, the biocompatibility, strong anticorrosion and antiwear properties, and mechanism of TiNi alloys are also described in detail. Several advanced manufacturing processes of TiNi alloys are also briefly outlined such as selective laser melting and spark plasma sintering. The performance of TiNi alloy coatings prepared by thermal spraying techniques are fully qualified for medical applications. Thermal spraying techniques have great prospects in reducing the cost and improving the quality of TiNi alloy medical products.

Keywords: biocompatibility; biomedical applications; corrosion; surface modification; TiNi alloys.

***Corresponding author: Qunfeng Zeng,** Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, China, e-mail: zengqf1949@gmail.com
Jianing Zhu: Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, China
Tao Fu: Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

1 Introduction

1.1 History and applications

Titanium (Ti) and its alloys are well known for their high corrosion resistance, low elastic modulus, and good biocompatibility, which are much better than those of stainless steel. Ti-based intermetallic alloys exhibit excellent high-temperature mechanical properties, significantly low density, good creep resistance up to 1000°C, and high oxidation resistance up to 900°C. TiNi alloys often play an important role in the biomedical field. Thus, they have been studied as biomaterials since their discovery by Buehler et al. (1963). The porosities of TiNi alloys have been investigated as an implant resource and tissue ingrowth. In fact, TiNi alloys are first used in orthodontic treatments and the bone plate. Gradually, this intermetallic alloy is used more and more widely. The scientific and technological development of TiNi alloy for biomedical applications is shown in Figure 1.

TiNi alloys are naturally studied as a medical and metal material with superelasticity, shape memory, and good biocompatibility. The first medical application was developed in 1971. Andreasen and Hilleman (1971) have implanted a TiNi alloy superelastic orthodontic device for the first time. After that, TiNi alloys have become more and more widely used in medical devices. The current research status of TiNi alloys in medical devices is introduced as follows. The application of TiNi alloys in the treatment of bone fracture was explored by Kang et al. (2002, 2005). They have designed and built bone holders using novel TiNi wires to design two bone holders for 20 patients. Continuous X-ray films, complete blood count, and urine analysis were performed without abnormalities after surgery. This clinical study demonstrated that TiNi alloys are suitable for bone fracture and provided new weapons for surgeons. Then, Szold (2006) pointed out the current status and developments of TiNi alloys in surgical applications. It was shown that TiNi alloy products have been widely used in medicine, such as self-expanding disc spacers made by TiNi alloys, vascular stents, and

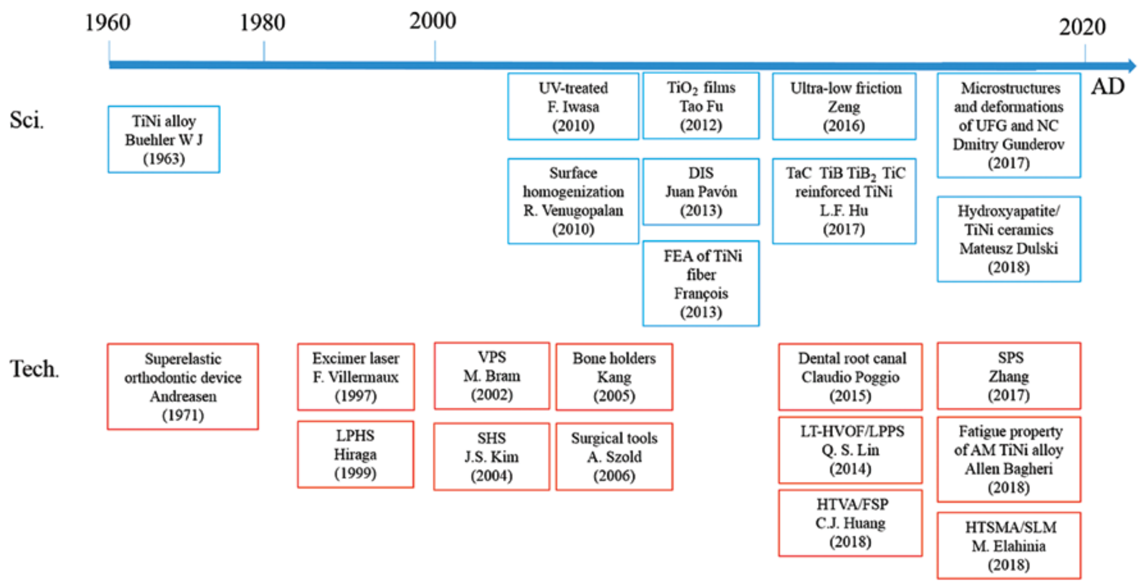

Figure 1: Development of the science and technology of TiNi alloys.

Nitinol anastomosis clips for left and right lateral anastomosis. It was also pointed out that the mechanical behaviors of TiNi alloys are nonlinear and there is a problem of hysteresis in the finite element modeling process, which will be gradually solved in future research (Tissot et al., 2013; Razali et al., 2016). Poggio et al. (2015) studied the applications of TiNi alloys in the treatment of dental root canal and fully evaluated the advantages and disadvantages of TiNi alloys in the manufacture of the root canal system.

At present, more than 1000 tons of Ti alloys have been implanted in patients worldwide (Batalu et al., 2014). However, the manufacturing cost of TiNi alloys increases gradually due to the increasingly complex part microstructures for biomedical applications. Therefore, the applications and researches of TiNi alloy coatings are more and more extensive in the field of biomedical applications.

In recent years, many researchers have studied a lot of work in the medical applications of TiNi alloy coatings. Thus, it is necessary to summarize the preparation methods, performance advantages, and medical applications to expand the medical applications of TiNi alloy coatings.

1.2 Structure and mechanical properties

The various properties of TiNi alloys, such as shape memory, corrosion resistance, superelasticity, are related to their internal metallographic structure (O'Brien et al., 2011). TiNi alloys produce a memory effect due to the phase transformations between martensite and austenite during stress or temperature changes as shown in Figure 2. TiNi alloy medical products, such as artificial joints, are inevitably subjected to force deformation

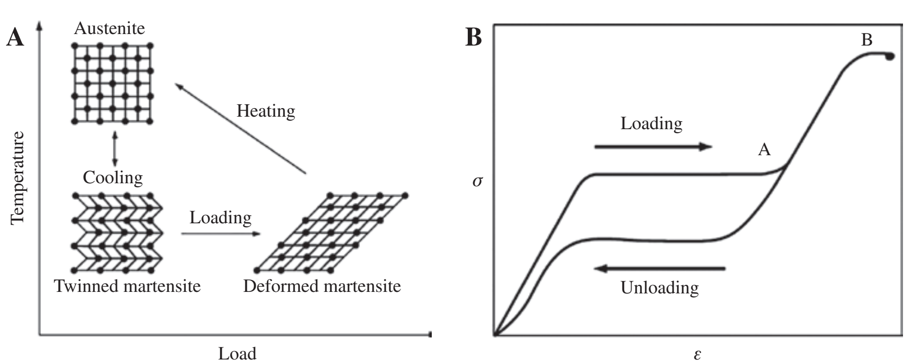

Figure 2: Shape memory of TiNi alloy: (A) thermal shape memory effect and (B) superelastic stress-strain behavior of NiTi (O'Brien et al., 2011). Copyright © Elsevier. License number 4556810296444.

during use. The temperature of TiNi alloys changes during use. However, the microstructures of TiNi alloys are affected by external forces and temperature. Changes in the microstructure and crystal structures of TiNi alloys result in changes in their properties, such as biocompatibility, shape memory, and other properties. Therefore, it is important to measure and study the microstructures of TiNi alloys.

There are generally two kinds of the crystal phases of TiNi alloys (Onda et al., 1992; Yamauchi et al., 1996; Mantovani, 2000): austenite and martensite. There are a large number of researches on the microstructures and types of twinning using transmission electron microscopy and high-resolution electron microscopy to characterize the interface of twinning at the nanometer scale (Nishida et al., 1995). The recoverable strain of TiNi alloy coatings is about 4.5% due to the devitrification and twinning process of martensite.

The initial states and microstructures of the annealed TiNi alloys were first studied in the wide temperature range by Kuntsevich and Pushin (2007) by transmission electron microscopy and X-ray diffraction technologies. The results showed that annealed TiNi alloys are formed to high-strength nanocrystals, and its martensite can undergo two kinds of transformation in B2 $\leftrightarrow$ R $\leftrightarrow$ B19′ and B2 $\leftrightarrow$ R.

Gunderov et al. (2017) studied the microstructures and deformations of ultrafine grain and nanocrystalline TiNi alloys produced by severe plastic deformation (Gunderov et al., 2013) after high-pressure torsion (HPT) and annealing. HPT-treated samples were annealed at 550°C, and their strengths decreased but ductility increased due to the martensitic transformation of B2 to B19′ occurring in TiNi alloys. The microstructures of TiNi alloys were changed into a ribbon microstructure using the ECAP-Conform technique to improve the tensile strength of TiNi alloys to 1300 MPa and a ductility of 25% (Churakova et al., 2017).

It was also pointed out that the mechanical behavior of TiNi alloys is nonlinear and there is a problem of hysteresis in the finite element modeling process. The CAE method such as finite element is gradually introduced to design medical TiNi alloy products. The finite element simulation of TiNi alloy elastomer composites used as biomaterials was studied by Tissot et al. (2013) to solve the problem of nonlinear behavior and hysteresis of TiNi alloys during finite element modeling. A homogenization method was proposed based on the geometry of TiNi alloy fiber. The superelastic properties, hardening behavior, hysteresis, and anisotropy of TiNi alloys were analyzed by the finite element method. The three-dimensional model of superelastic TiNi alloy archwire in the orthodontic three-stent system was developed by Razali et al. (2016) using the finite element method to achieve an online measurement of the frictional force and the restoring force of the tooth movement in the stent system. The prediction of the bending model is in good agreement with the experimental results.

Good mechanical properties are required to meet the life and reliability requirements of the biomedical products. TiNi alloys are proven to have high wear resistance and low coefficient of friction, and the fatigue resistance of TiNi alloys is much better than traditional bioceramic materials. Therefore, it is necessary to investigate the mechanical properties of TiNi alloy coatings to expand the applications of TiNi alloy coatings in biomedical applications.

2 Bulk TiNi alloy

2.1 Biomedical properties and surface modification

Determining whether a material is suitable for biomedical applications requires the performances to meet biocompatibility, bioadhesion, biofunctionality, and corrosion resistance. TiNi alloys are materials with great potential for biomedical applications due to their excellent performances (Bombac et al., 2007; Clarke et al., 2010). However, it has a certain resistance in the applications as a biomedical material due to the possible corrosion in physiologic solutions and the dissolution of carcinogenic Ni elements. Therefore, it is necessary to investigate the surface modification of TiNi alloy coatings in depth to improve the biocompatibility of TiNi alloy coatings.

Since the 1990s, many researchers have conducted specific researches about this topic. The TiO_2 oxide layer plays an important role in the surface of TiNi alloys as a bioinert material. The oxide layer prevents Ni atoms from diffusing into the blood and improves the corrosion resistance of TiNi alloys (Firstov et al., 2002; Shabalovskaya, 2002; Tao et al., 2012).

TiNi alloys were investigated for cytotoxicity by Sevcikova and Goldbergova (2017). The investigators used sulforhodamine B assays (Gill et al., 2015), MTT assays (Bernard et al., 2011), expression profiles (Lu et al., 2009), and cell survival assays such as apoptosis assays to assess cytotoxicity (Yeung et al., 2010). Although the biocompatibility of TiNi alloys is still controversial to date, almost all data about the surface is a very good biomedical material.

2.1.1 Corrosion and surface modification

Corrosion is one of the most important factors determining the biocompatibility of TiNi alloys due to a large amount of Cl ions in body fluids. In complex body fluid environments, TiNi alloys are still subjected to wear and corrosion, which leads to the leaching of toxic and carcinogenic Ni elements. Therefore, improving the corrosion resistance of TiNi alloys has been extensively studied.

The surface treatments of TiNi alloys were studied by Villermaux et al. (1996, 1997), and the surface of TiNi alloys was treated by the excimer laser. In Figure 3, the treated surfaces are subjected to much lower corrosion than the untreated surface. The surface of TiNi alloys is homogenized by laser surface melting, and the N element penetrates into the surface of TiNi alloys, causing the hardening of TiNi alloys and the thickening of the oxide layer.

The surface homogenization treatment of TiNi alloys was studied by Venugopalan and Trepanier (2000), Shabalovskaya (2001), and Santipach and Honig (2010). The results showed that the passivated and electrolytically polished TiNi alloy disk is more resistant to static corrosion and repassivation (repair ability) than other biomedical materials, and the release of Ni is far below the dietary level.

Shabalovskaya et al. (2004) compared the corrosion properties of medical TiNi alloy wires treated by sand blasting and smooth fine-drawing with alloy wires with black oxide on the surface during the manufacturing process in 0.9% NaCl solution. The studies showed that blasting and smooth fine-drawing are not very effective at the original scale, even exacerbating long-lasting scaling and greatly reducing the corrosion resistance. The reason is that the local defects generated after blasting and smooth fine-drawing lead to the unevenness of the alloy surface, thereby causing local corrosion. Therefore, eliminating the unevenness of the surfaces is an important direction to improve the corrosion resistance of TiNi alloys.

The corrosion resistance of pulsed high-energy density plasma (PHEDP)-modified TiNi alloys was studied by Fu et al. (2000). It was found that TiN nanocrystalline films are formed on the surface of PHEDP-modified TiNi alloys. Due to the plasma films, the size of the TiNi crystal grains was reduced, the adhesion of TiN nanocrystalline films on TiNi alloys was improved, and the corrosion resistance was greatly improved. Tan et al. (2003) used plasma implantation to improve the corrosion resistance of TiNi alloys. TiNi alloys were implanted by oxygen ions at 45 kV, and it was found that the sample had the best corrosion resistance at 21°C at an ion concentration of 1×10^{17} ions/cm^{-2}. Carbon plasma immersion ion implantation (C-PIII) was performed for 2 h to improve the corrosion resistance of TiNi alloys by Shanaghi and Chu (2018). Electrochemical impedance spectroscopy indicated that C-PIII improves the pitting or local corrosion resistance of TiNi alloys.

Corrosion of TiNi alloys *in vivo* causes the precipitation of Ni, which leads to allergies or carcinogenesis. Corrosion resistance is effectively enhanced by surface homogenization or surface ion implantation, which eliminates the unevenness or generates the reinforcing phase. The precipitation of Ni *in vivo* is effectively prevented by these methods.

2.1.2 Biocompatibility and surface modification

Biocompatibility is one of the most important properties for measuring the response of the living tissue to inactive materials. The interaction between TiNi alloys and tissue are balanced when the alloys are implanted into the human body. Therefore, it is important to improve the biocompatibility of TiNi alloys.

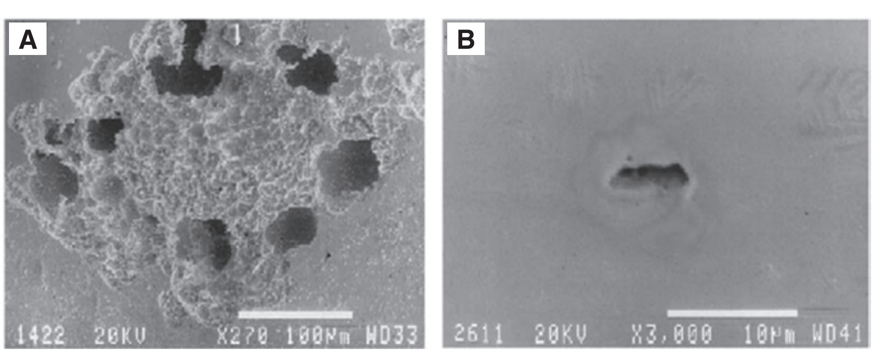

Figure 3: Scanning electron microscopy of (A) corroded untreated plate and (B) corroded treated pate (Villermaux et al., 1997). Copyright © Elsevier. License number 4554800640225.

Firstov et al. (2002) conducted an experimental study on the oxidation mechanism of TiNi alloy surfaces. The surface of TiNi alloys after mechanical polishing was treated at temperatures of 300°C–800°C, and it was found that a smooth protective Ni-free oxide layer was formed at the treatment temperature of 500°C. Santipach and Honig (2010) studied the effect of electropolishing on the biocompatibility of TiNi alloys further. The results showed that when a mixed solution of sulfuric acid and hydrofluoric acid is used as the electrolyte, a uniform morphology surface is obtained, and a uniform TiO_2 layer is formed, which further improves the corrosion resistance and biocompatibility of TiNi alloys. Michiardi et al. (2007) also demonstrated that oxidation treatment could improve the adsorption efficiency of proteins and the biocompatibility from the surface energy point of view through oxidation treatment.

The bioactivity mechanism of ultraviolet (UV)-treated Ti alloys was studied by Iwasa et al. (2010). The osteoblasts produced in the rat bone marrow were distributed on untreated and UV-treated Ti alloys, and it was found that the UV-treated Ti alloys changed from hydrophobic to hydrophilic and had better biological activity. Because TiO_2 is irradiated with UV light, its electrons are excited from the valence band to the conduction band, so it is positively charged and more easily combined with proteins and cells (mostly anions), making the Ti alloy more biocompatible.

In addition, the surface roughness of TiNi alloys also affects the growth of cells on its surface. Samaroo et al. (2008) synthesized various TiNi alloy substrates with different microsurface to nanosurface roughnesses using different compositions of TiNi alloy powders. The results showed that the cells adhere much better and proliferate faster on finer particles. Tissue scaffolds of TiNi alloys were fabricated using directed irradiation synthesis (DIS) technology by Pav et al. (2013). This novel nanostructured surface allows cells to attach well.

Dulski et al. (2018) sintered hydroxyapatite and TiNi alloy powders into mixed ceramics. Combining the good biocompatibility of both and the mechanical properties of TiNi alloys compensates for the poor mechanical properties (brittleness, low tensile strength, and poor impact resistance) of phosphate. Phosphate ceramics as an auxiliary material can improve the corrosion resistance of metals and inhibit the release of toxic metal ions into organs.

The influence of the surface oxide of TiNi alloys on its corrosion resistance was studied by Fu et al. (2012). A film with nanopores was prepared by the solution gel method on TiNi alloy substrates pretreated by NaOH-HCl solution. The potentiodynamic polarization test in 0.9% NaCl solution shows that TiNi alloys with TiO_2 films have excellent corrosion performances and some controllable preparations of corrosion-resistant TiNi alloys are achieved.

Conventional TiNi alloy materials were modified through DIS by Hench and Polak (2002), Pav et al. (2013), and Dulski et al. (2018). The modified nanostructures provide the optimal adhesion to cells and reduce the hydrophobicity by 20%–40%. A variety of surface treatment methods were evaluated to modify the hydrophilic nature of TiNi alloy coatings by Chun et al. (2009). It was suggested that increasing the hydrophilicity reduces the prevalence of platelet adhesion and thrombosis in the vascular system. The superhydrophilic surface was formed by two surface treatments: after thermal treatment at 600°C for 30 min and 30% hydrogen peroxide treatment for 15 h. However, the superhydrophilic films treated by thermal are embrittled due to the relative thickness of the grown oxide films.

The surface oxide layer is the main factor affecting the biocompatibility of TiNi alloys. The TiO_2 layer is formed in situ by the surface modification of TiNi alloys. It is also able to prepare TiO_2 coatings directly on the surface of TiNi alloys by the solution gel method. Therefore, increasing the thickness of the oxide layer on the surface of TiNi alloys is the main research direction to improve its biocompatibility.

2.2 Superlubrication (friction behaviors)

TiNi alloy biomedical products, such as artificial joints, are subjected to extreme loads during use. For example, a hip prosthesis can withstand 1–2 million cycles per year with articulating forces reaching three to five times the body weight (Brunette, 2001). Artificial joints produced abrasive particles under great friction and fatigue during use, resulting in the failure of the component. TiNi alloys have better mechanical properties such as friction and fatigue properties than traditional ceramic materials. Therefore, it is necessary to study the wear behaviors and other mechanical properties of TiNi alloys in detail.

TiNi alloy coatings have been used in recent years for joint replacement, dental shaping, and skeletal orthodontics due to their good biomedical prospects (Hussein et al., 2015). TiNi alloy coatings are increasingly used in artificial joints and other applications due to their low friction behaviors. Antiwear behavior is the main factor that controls and determines the stability and reliability of biomaterials in long-term clinical applications. In 2003, the abrasive wear of TiNi alloys was studied by Imbeni et al. (2003). As the grain size of the abrasive increases and the roundness factor decreases, the surface roughness of TiNi alloy article increases. The cracks of many medical devices are usually less than 25 μm. Thus, it is necessary to further study the grinding media and the grinding process of less than 20 μm.

It is also necessary to reduce the friction coefficient of TiNi alloy coatings to prevent the generation of abrasive grain particles. As for the tribological properties of TiNi alloys, many researches have been carried out in recent years. The tribological properties of TiNi alloys under liquid lubrications were systematically studied by Zeng (2013), Zeng and Dong (2014), and Zeng et al. (2016), and low coefficient of friction was achieved. In the case of castor oil, the ultra-low friction coefficient of 0.008 was obtained. The ultra-low friction mechanism is attributed to the OH-terminated surface generated by friction-induced castor oil degradation, and the contact surface of the friction pair formed a boundary lubricating film, which lowers the friction coefficient.

The friction and wear behaviors of TiNi alloy coatings in biomedical applications are far less than those of bulk TiNi alloys. Therefore, the friction behaviors of TiNi alloy coatings are studied in depth to improve the reliability and service life of TiNi alloy-coated products.

2.3 TiNi composites

In general, the single TiNi alloy has difficulty to meet the mechanical properties of parts in the biomedical field. Therefore, the mechanical properties of TiNi alloys are often improved by the method of preparing TiNi composites.

The corrosion behavior of TiNi alloys in Cl-rich solution was investigated by Hu et al. (2017). The reinforcing phase of TaC was added to TiB, TiB_2, and TiC reinforced Ti_2Ni/TiNi composite coatings, which greatly improves the corrosion resistance of the composite coatings in Cl-rich solution.

Fatigue refers to an important consideration in the work of TiNi alloy products. During the entire working life of medical products such as prostheses, TiNi alloys are subjected to the repeated cyclic loads. The fatigue performance of Ti coatings on Ti6Al4V alloy substrate under cold gas dynamic spraying (CGDS) was studied by Price et al. (2006). However, it is found that the fatigue properties of the substrate were reduced due to changes in the surface topography of the substrate and the participation in the tensile stress in the substrate caused by the CGDS process. Filip et al. (1999) prepared TiNi/Al_2O_3/Ti alloy composites and studied the structure and properties of TiNi/Al_2O_3/Ti composites to improve the fatigue properties of TiNi alloys. The fatigue life of this new composite material is greater than 10^7 cycles; thus, the mechanical properties meet the application of bone tissue treatment.

The fatigue performance of TiNi alloys is improved by reducing friction between human tissue and the surface of the part. TiNi endodontic files (EFs) used for root canal treatment were coated by Adini et al. (2011) with cobalt films containing fullerene-like WS_2 nanoparticles, which can improve the fatigue resistance of the TiNi EFs.

TiNi alloys have been widely used in the field of medical devices because of its biocompatibility, corrosion resistance, superlubrication, shape memory effects, and so on. TiNi alloys have been used in the manufacture of minimally invasive implants, orthopedic instruments, dental instruments, and sutures.

Grunert et al. (2016) described the development of orbital floor implants made by TiNi alloys. The alloy can be used for the treatment of orbital fractures as shown in Figure 4, which are inserted in the eye socket through an open approach on the lower eyelid.

3 TiNi alloy coatings

The applications of TiNi alloys have become more widespread with the development of TiNi alloys. TiNi alloys are usually used as substitutes for bones due to their good biocompatibility. However, structures such as bones are very complicated and difficult to be obtained by mechanical processing. Moreover, the production cost is usually reduced by spreading TiNi alloy coatings due to the high processing cost of pure Ti alloys (He et al., 2000). The cutting behaviors of TiNi alloys are studied by Lin et al. (2000), Wu et al. (1999), and Weinert and Petzoldt (2003). It is found that TiNi alloys are difficult to be processed due to highly viscous and pseudo-elastic properties. Long processing time, strong adhesion of TiNi alloy fragments, and the wear of tools are still high even under optimized cutting parameters. The manufacture of large TiNi components is also limited by the high costs and difficulties of manufacturing, except for the extensive performance of the widely discussed TiNi alloys. Thermal spraying technology has no restrictions on the structure of the part, and it can spray onto complex biomedical parts. Therefore, the

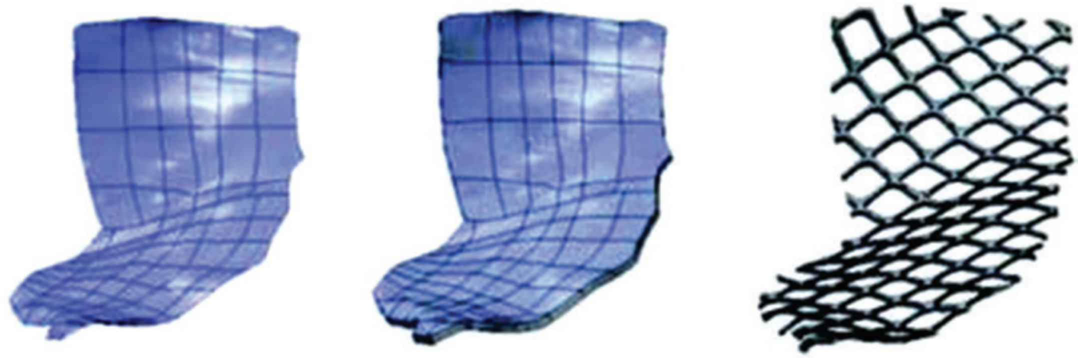

Figure 4: Stages of the planned implant. A surface model (left) is derived from the computed tomography data, picturing the patient-specific geometry. With the help of a three-dimensional model (middle), the implant with the grid structure is made individually (Grunert et al., 2016). Copyright © Elsevier. License number 4555230145843.

thermal spraying technology of TiNi alloys is gradually studied and applied.

3.1 Preparation of coatings

3.1.1 Flame spraying/explosive spraying/low-temperature high-velocity oxygen fuel spraying (LT-HVOF)

Richman et al. (1995) studied the performances of TiNi alloy coatings by explosive spraying. It was found that the martensite in TiNi alloy coatings is beneficial to improve the corrosion resistance of TiNi alloys, whereas the corrosion resistance of austenite is significantly enhanced after welding, but the corrosion loss is restored at the heating temperature of 500°C for 15 min after welding.

The deposition mechanism and oxidation behaviors of Ti-Ni deposited during LT-HVOF spraying process were studied by Lin et al. (2014a,b). TiNi alloy coatings deposited by TiNi intermetallic compound powder using LT-HVOF spraying process have a typically layered microstructure and a very low porosity. Ni-coated Ti powder can be used to produce low-oxygen dense TiNi alloy coatings.

3.1.2 Laser plasma hybrid spray coating (LPHS)/vacuum plasma spraying (VPS)/low-pressure plasma spraying (LPPS)

Hiraga et al. (1999) studied the cavitation mechanism of TiNi alloy coatings by LPHS. The corrosion resistance of TiNi alloy coatings is improved because Ni reduces the phase transition temperature of austenite to martensite with the increase in Ni content. Then, the corrosion resistance of TiNi alloy coatings sprayed by VPS and laser plasma hybrid spraying (LPHS) was studied. The corrosion resistance of two TiNi alloy coatings sprayed by VPS and LPHS methods was 20 and 40 times, respectively, more than ordinary Ti coatings (Hiraga et al., 2001). The preparation of TiNi alloy coatings by VPS was further studied by Bram et al. (2002). TiNi alloy coatings were prepared using 50.8 at% of Ni alloy powder as shown in Figure 5. After heat treatment at 900°C for 2 h, the microstructures

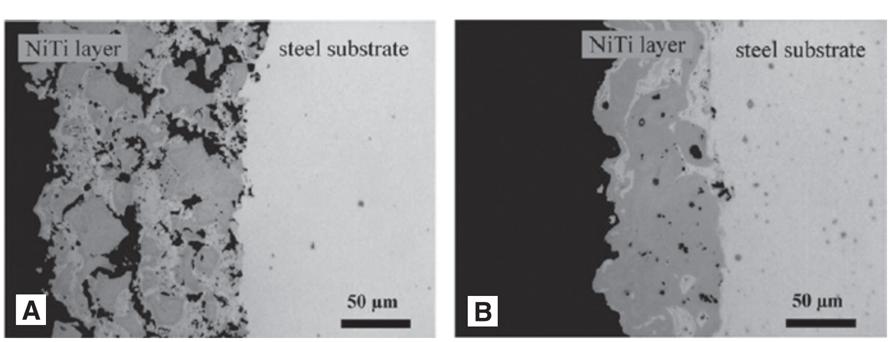

Figure 5: TiNi alloy coatings on a steel substrate produced by VPS (Bram et al., 2002). (A) The coating is porous and inhomogeneous. (B) The coating is less porous and exhibits a higher homogeneity. Copyright © Elsevier. License number 4555250429975.

of TiNi alloy coatings became uniform, but pure Ni phase still existed. It is well known from biomedical investigations that the existence of pure Ni promotes the appearance of an allergy or leads to allergic reactions, such as the latent inflammation of the surrounding tissue if the allergy has already presented (Bram et al., 2002). Measurements of the wear resistance of TiNi alloy coatings in the as-sprayed state and after annealing are the subjects of further investigations.

The applications of LPPS in the preparation of TiNi alloy coatings were also studied (Lin et al., 2014a,b). Ni-coated Ti powders were used as raw materials for preparation, and the results showed that the cavitation resistance of TiNi alloy coatings is superior to 316L stainless steel.

3.1.3 Arc sprayed/cathodic arc-ion plating (CAP)

The arc-sprayed TiNi alloys were studied by Jardine et al. (1990). The results showed that arc spraying is feasible for the preparation of TiNi alloy coatings and the ductility and memory effects of the coatings are improved by vacuum annealing.

CAP in the preparation of TiNi alloy coatings was studied by He et al. (2000). The results showed that high-quality TiNi alloy coatings are obtained using CAP technology and deposited without heat treatment when the negative bias is enough.

3.1.4 Self-propagating high-temperature synthesis (SHS)

High-porosity TiNi alloy coatings were successfully prepared through SHS by Li et al. (2000) and Kim et al. (2004, 2010a,b). The phase changes and the macroscopic distributions of the pores were adjusted by the preheating temperatures.

3.1.5 Magnetron sputtering

Magnetron sputtering is commonly used to prepare TiNi alloy coatings. TiNi shape memory films were obtained at low temperature by DC magnetron sputtering by Cicek et al. (2015), as shown in Figure 6. Crystalline TiNi films were obtained by high sputtering current, low working pressure, and high substrate pulse (Figure 6A). TiNi and TiNiAg coatings were obtained through magnetron sputtering technique by Quandt and Zamponi (2008). The utilization of melt-cast sputtering targets followed by annealing in a rapid thermal annealing apparatus led to crystalline films. These TiNi films revealed superelastic properties at a temperature of 36°C.

3.2 Surface modification of TiNi alloy coatings

TiNi alloy coatings directly prepared often have many disadvantages such as insufficient hardness or poor corrosion resistance. Therefore, surface modification is necessary to improve the performance of TiNi alloy coatings.

Richman et al. (1995) and Hiraga et al. (1999) produced TiNi alloy coatings by explosive spray and laser hybrid composite spraying (LPHS), respectively. The results showed that the martensite of TiNi alloys is beneficial to improve the corrosion resistance of TiNi alloy coatings.

The deposition of nanocrystalline TiN protective coatings on the surface of TiNi alloy coatings by DC magnetron sputtering was discussed by Kumar and Kaur (2009). The modified TiNi alloy coatings exhibit high hardness and modulus of elasticity, good wear resistance, and corrosion

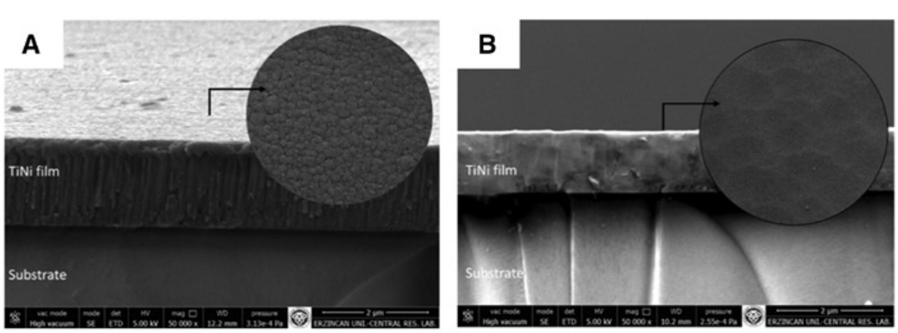

Figure 6: Surface and cross-section images of TiNi films: (A) crystalline films and (B) noncrystalline films (Cicek et al., 2015). Copyright © Elsevier. License number 4556390138610.

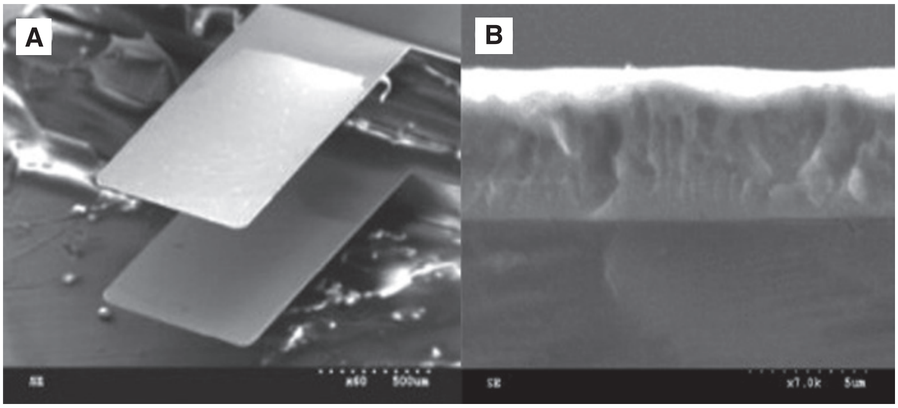

Figure 7: (A) Assembled medium-sized microgripper and (B) cross-section (Fu et al., 2001). Copyright © Elsevier. License number 4555650080131.

resistance. At the same time, applications of TiN/TiNi films in the electrochemical sensing of dopamine have been proven, which have important physiologic research prospects in the treatment of Parkinson's disease.

Tillmann and Momeni (2014) deposited superelastic TiNi coatings on an Si (100) substrate by DC magnetron sputtering and applied the TiCN coatings to the austenitic TiNi alloy coatings to improve the corrosion and wear resistance. The original TiNi alloy coatings were transformed into a new generation of self-healing composite TiNi alloy-based films, which have great reference values for the biomedical applications of TiNi alloy coatings.

High-temperature vacuum annealing and friction stir processing were employed to modify cold-sprayed TiNi coatings obtained from a mechanically blended powder by Huang et al. (2018). The microhardness of the improved layer was increased to $1003.5 \pm 65.9\ HV_{0.1}$, which is about 4.5 times compared to the TiNi coating prepared by cold spraying ($222.5 \pm 6.6\ HV_{0.1}$).

At present, TiNi alloy coatings have been widely used in the medical field to reduce cost. The microgripper was fabricated by Huang et al. (2003) and Fu et al. (2001) and consisted of two cantilever beams made of Si and coated with TiNi alloy coatings as shown in Figure 7. The manufacturing cost of microgripper is greatly reduced because TiNi alloy coatings are deposited on the top of the Si wafer by sputtering.

Thin-film TiNi shape memory alloy (SMA) microactuator was prepared by Gill et al. (2001) through magnetron sputtering and wet etching. The purpose of the microactuator is to grab microsize objects such as cancerous tumor for removal from the body. As shown in Figure 8, TiNi alloy thin films were deposited by magnetron sputtering. These devices are successfully employed to pattern cylindrical TiNi alloy thin films used for the stent.

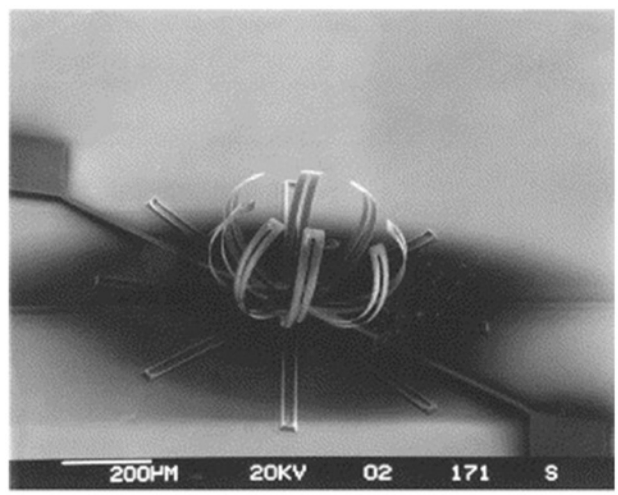

Figure 8: Fabricated microwrapper with TiNi alloys (Gill et al., 2001). Copyright © Elsevier. License number 4556940290099.

4 Advanced manufacturing process of TiNi alloy

With the increasingly complex microstructure of TiNi alloy biomedical parts, additive manufacturing technology of TiNi alloys has gradually become a research hotspot in recent years (Elahinia et al., 2016).

Selective laser melting (SLM) was studied in the preparations of TiNi alloy biomaterials by Huang (2008). The results showed that SLM parts have defects such as incomplete melting, thermal deformation, and spheroidization, but choosing the right laser mode and scanning form ensures the quality of the finished parts. An NiTi-20Hf high-temperature SMA was additively manufactured and the shape memory properties were characterized by

Elahinia et al. (2018). The composition analysis shows Ni loss and O gain after SLM processing due to the associated high-power laser melting. In addition, finely dispersed particles, pores, and cracks were observed after SLM.

The fatigue properties of 3D printed TiNi alloys were studied by Elahinia et al. (2018). However, fatigue resistance is still low and further exploration is proposed to reduce the cost of TiNi alloys in medical applications compared to TiNi alloy parts manufactured by the traditional method. Control of grain size is critical to improve the performance of TiNi alloys by additive manufacturing. The influence of laser power, scanning speed, and laser path onto the microstructure of TiNi cylinders was studied by Bormann et al. (2014). Control of scanning speed allows the restricted changes of the transformation temperatures, and control of laser power and scanning path makes the microstructures, such as crystallite shapes and arrangement, extent of the preferred crystallographic orientation, and distribution of the grain size, tailor-made.

The functional-structural NiTi/hydroxyapatite (NiTi/NA) composite with enhanced mechanical properties and high biocompatibility was fabricated through spark plasma sintering (SPS) by Zhang et al. (2017) as shown in Figure 9. The nanosized HA and pores improve the biocompatibility without deteriorating the mechanical properties and superelasticity. This work means that the composites are promising as bone implants.

With the development of additive manufacturing technology, more and more complex parts are manufactured (Habijan et al., 2013), as shown in Figure 10. In the

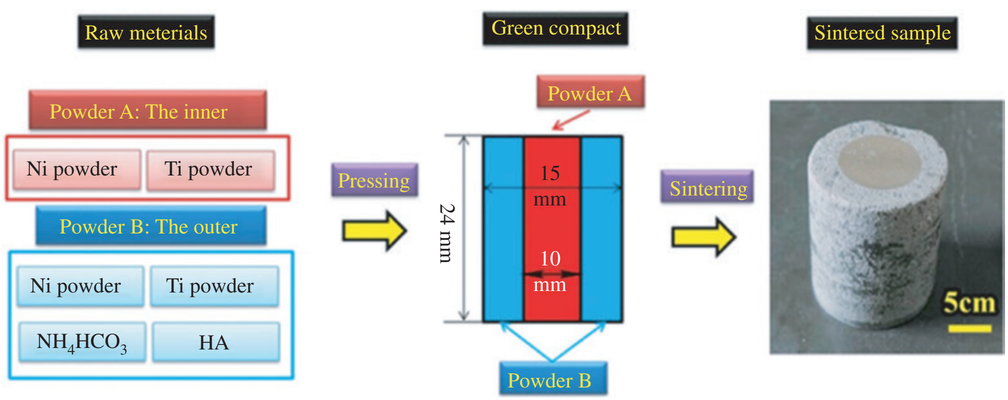

Figure 9: Schematic sketch of the composites fabricated by SPS (Zhang et al., 2017). Copyright © Elsevier. License number 4555360642399.

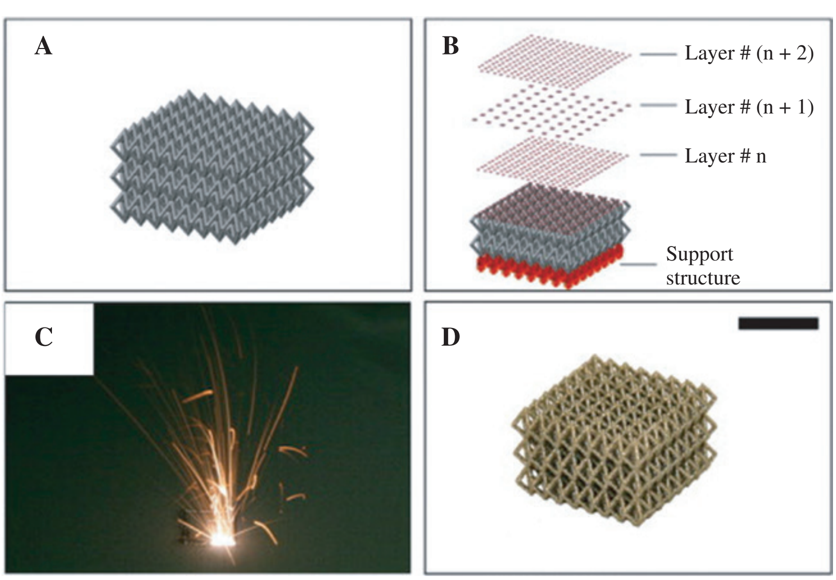

Figure 10: SLM procedure: (A) CAD model of the later part, (B) CAD model prepared for SLM, (C) laser-material interaction during SLM, and (D) finished NiTi-SLM structure (Habijan et al., 2013). Copyright © Elsevier. License number 4555831459318.

field of biomedicine, additive manufacturing technology will have more applications.

5 Summary and remarks

5.1 Summary

(1) Precipitation of Ni is essential to weaken the biomedical properties of TiNi alloys. Surface modification is an effective method to prohibit the precipitation of Ni and improve the biomedical properties of bulk TiNi alloys. Corrosion resistance is enhanced by eliminating the unevenness or generating the reinforcing phase through surface homogenization or surface ion implantation. The TiO_2 layer is the main factor that affects the biocompatibility of TiNi alloys. Increasing the thickness and density of the TiO_2 layer on the surface of TiNi alloys is an important method to improve the biocompatibility.

(2) TiNi alloys are widely used in biomedical applications, but there are difficult-to-process metal materials due to their viscosity and pseudo-elasticity during processing, resulting in an increase in the cost of using. Therefore, the manufacturing process of TiNi alloy coatings has been gradually studied. Thermal spraying technology has shortcomings, but the ductility and memory of TiNi alloys are restored by vacuum annealing treatment. The strength and corrosion resistance of TiNi alloy coatings are enhanced by the decrease in the transformation temperature of austenite to martensite and increase in the proportion of martensite. Currently, TiNi alloy coatings prepared by LPHS have excellent corrosion resistance.

5.2 Remarks

With the development of surface modification technology, the biomedical properties of TiNi alloys are continuously improved. However, the application of bulk TiNi alloys is limited by high processing cost. Researches on the preparations of TiNi alloy coatings not only help to reduce the manufacturing cost of TiNi medical products but also contribute to process parts with more complex shapes. In addition, advanced manufacturing technologies such as additive manufacturing or powder metallurgy are also used to manufacture TiNi alloys. Therefore, further research of the biomedical applications of TiNi alloys is needed.

(1) The oxidation mechanism of TiNi alloys is further investigated systematically, and a new process of surface homogenization is proposed to improve the corrosion resistance of TiNi alloys. Improving the thickness of the oxide layer on the surface of TiNi alloys is studied in detail to enhance the lifetime and reliability of TiNi alloy medical products.

(2) Reducing the grain size and surface roughness of TiNi alloy coatings is studied to improve blood compatibility and hydrophilicity and reduce thrombus formation.

(3) The phase transition mechanism of TiNi alloys is studied in detail to improve the quality of TiNi alloy products made by additive manufacturing technology.

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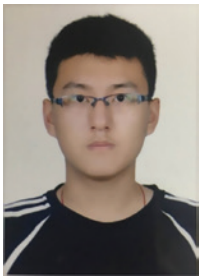

Jianing Zhu
Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Jianing Zhu is a doctoral student at the School of Mechanical Engineering, Xi'an Jiaotong University, China. His main research is the design of coatings of NiTi alloys, DLC films, and other ceramic materials for high-temperature lubrication and corrosion prevention.

Qunfeng Zeng
Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, China, **zengqf1949@gmail.com**

Qunfeng Zeng is an associate professor at the School of Mechanical Engineering, Xi'an Jiaotong University, China. He lectures on mechanical engineering and is dedicated to research on coatings for mechanical engineering applications. His main research is the sealing, wear, lubrication, and corrosion mechanisms and control methods of NiTi alloys, steels, DLC films, and other anticorrosion and lubricating materials.

Tao Fu
Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

Tao Fu is an associate professor at the School of Life Science and Technology, Xi'an Jiaotong University, China. He lectures on biomaterials science and is involved in the research of coating technologies for biomedical and engineering applications. His research includes physical vapor deposited, plasma sprayed, and chemically prepared coatings for corrosion protection, mechanical enhancement, and functionalization of stainless steels, Ti alloys, NiTi alloys, and other metallic materials.