

## Review Article

# Brief Overview on Nitinol as Biomaterial

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Shape memory alloys remember their shape due to thermoelastic martensitic phase transformation. These alloys have advantages in terms of large recoverable strain and these alloys can exert continuous force during use. Equiatomic NiTi, also known as nitinol, has a great potential for use as a biomaterial as compared to other conventional materials due to its shape memory and superelastic properties. In this paper, an overview of recent research and development related to NiTi based shape memory alloys is presented. Applications and uses of NiTi based shape memory alloys as biomaterials are discussed. Biocompatibility issues of nitinol and researchers' approach to overcome this problem are also briefly discussed.

## 1. Introduction

*1.1. Biomaterial.* Biomaterials are those materials that are used in the human body. Biomaterials should have two important properties: biofunctionality and biocompatibility [1]. Good biofunctionality means that the biomaterial can perform the required function when it is used as a biomaterial. Biocompatibility means that the material should not be toxic within the body. Because of these two rigorous properties required for the material to be used as a biomaterial, not all materials are suitable for biomedical applications. The use of biomaterials in the medical field is an area of great interest as average life has increased due to advances in the use of surgical instruments and the use of biomaterials [2]. In vivo testing is related to testing within a living organism and in vitro testing is related to testing in an artificial environment. There are many famous journals related to biomaterials, for example, Biomaterials, Acta Biomaterialia, Journal of the Mechanical Behavior of Biomedical Materials, and Journal of Biomaterials Applications.

*1.2. Shape Memory Alloys.* Shape memory alloys have the ability to recover their original shape [3, 4]. Shape memory alloys remember their original shape. Figure 1 shows the mechanism of shape memory effect. Details about this figure are also available in the current author's Ph.D. thesis [5]. The mechanism of shape memory effect and change in lattice

structure is also given in Figure 8 of [6]. Here, the parent austenite phase is stable above austenite finish temperature and transforms to diffusionless twinned oriented martensitic phase upon cooling to a temperature below the martensite finish temperature ( $M_f$ ). In this process, the macroscopic shape of the specimen remains the same as the diffusionless martensitic phase transformation is self-accommodating [7]; however, microscopic changes take place during phase transformation. For shape memory effect, the material in general is in martensitic state at test temperature. When we apply an external force, martensite changes to detwinned martensite. Upon removal of force, the material becomes in detwinned martensitic state. When we heat this material above the austenite finish temperature ( $A_f$ ), reverse transformation occurs from detwinned/deformation-induced martensite to parent phase and the original shape is recovered. This is the mechanism of shape memory effect (SME). In case of shape memory effect, heating above the austenite transformation temperatures is a must to recover the original shape [5, 8].

*1.3. Superelasticity.* Figure 2 shows the mechanism of superelasticity. In case of superelasticity, the test temperature in general is well above the austenite finish temperature or in between the austenite start ( $A_s$ ) and austenite finish ( $A_f$ ) temperatures and the material is in austenitic state at test temperature. When we apply force, this austenite transforms to stress induced martensite. However, this martensite is

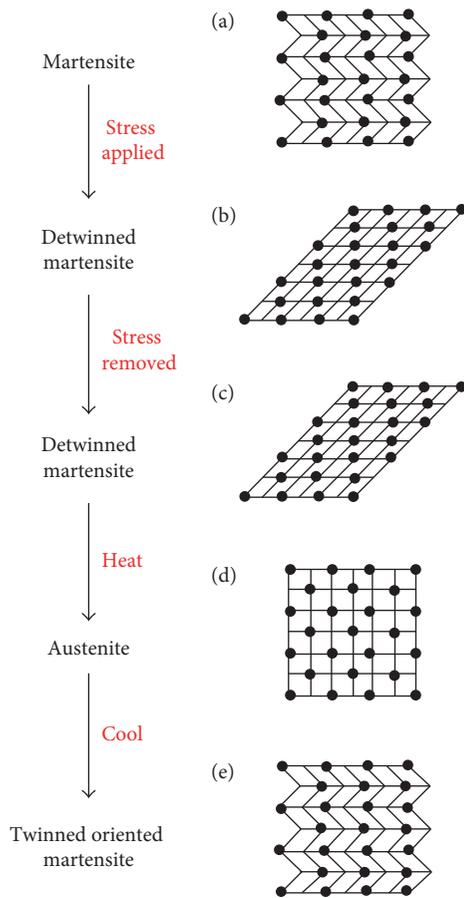


FIGURE 1: Mechanism of shape memory effect when test temperature is below  $M_f$ . (a) Martensite at test temperature. (b) Detwinned martensite upon application of stress. (c) Detwinned martensite upon removal of stress. (d) Austenite upon heating above  $A_f$ . (e) Martensite upon cooling below  $M_f$  (test temperature). Change in lattice structure with phase transformation is given in Figure 8 of [6].

stable only under the application of stress, and when we remove the stress, the material reverts back to austenite. In case of superelasticity, heating is not required to recover the original shape as here martensite is stable only under the application of stress [3, 8, 9].

**1.4. Transformation Temperatures and Their Importance.** The most effective and widely used shape memory alloys are nitinol [3, 7–12], copper based shape memory alloys [13–15], and iron based shape memory alloys [16–18]. Applications of shape memory alloys depend upon their phase transformation temperatures. These transformation temperatures are martensite start temperature ( $M_s$ ), martensite finish temperature ( $M_f$ ), austenite start temperature ( $A_s$ ), and austenite finish temperature ( $A_f$ ) [3]. Transformation temperatures of nitinol are well below or close to body temperature, which is why nitinol has a large number of applications as a biomaterial [19–21] compared to copper based and iron based shape memory alloys where transformation temperatures are well above the body temperature [13–18]. Copper based shape

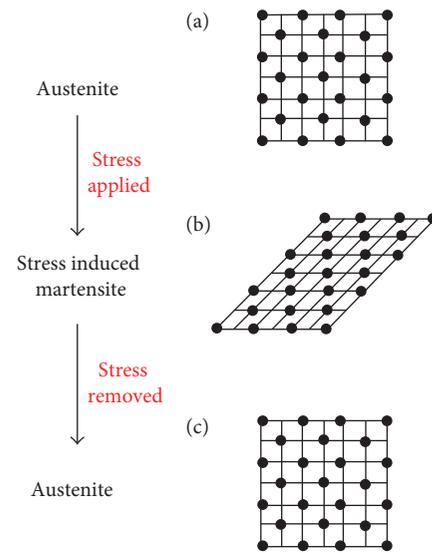


FIGURE 2: Mechanism of superelasticity when test temperature is above  $A_f$ . (a) Austenite at test temperature. (b) Stress induced martensite upon application of stress. (c) Austenite upon removal of stress. Change in lattice structure with phase transformation is given in Figure 8 of [6].

memory alloys are suitable for high temperature,  $\sim 473$  K, applications; however, due to above-body-temperature transformation temperatures, these alloys are not suitable as a biomaterial [13–15]. There is a need for research on copper based shape memory alloys to decrease their transformation temperatures below body temperature so that these alloys can be used as a biomaterial. Transformation temperatures dictate the use of shape memory alloy. If austenite transformation temperatures are below the body (test) temperature, then the shape memory alloy can be used as a biomaterial due to its superelasticity, and if the test temperature is below the martensitic transformation temperatures, then shape memory alloy can be used as a biomaterial due to its shape memory effect [3, 22].

**1.5. Nitinol.** Nitinol is a family of titanium based intermetallic materials that contain nearly equal amount of nickel and titanium. Nitinol shows shape memory and superelastic properties due to thermoelastic martensitic transformation [3, 7, 12]. In near-equiatomic NiTi alloys, shape memory effect and superelasticity are due to thermoelastic martensitic transformation from parent austenite phase with B2 structure to the monoclinic (M) or rhombohedral (R) martensitic phase transformation [23–25]. Table 1 shows different phases of equiatomic NiTi shape memory alloy, crystal system, lattice parameters, and interaxial angles. NiTi shape memory alloys were discovered by William J. Buehler and his coworkers in 1963 in the Naval Ordnance Lab (NOL), which is why equiatomic NiTi shape memory alloy is more commonly known as “nitinol” where “niti” stands for nickel-titanium and “nol” stands for Naval Ordnance Lab (NOL) [10, 26].

Phase diagrams are very important in studying different alloy systems, composition and temperature dependent

TABLE 1: Different phases of equiatomic NiTi shape memory alloy, crystal system, lattice parameters, and interaxial angles.

NiTi	Crystal system	Lattice parameters	Interaxial angles
Austenite	B2, ordered BCC	$a = b = c$	$\alpha = \beta = \gamma$
Martensite (M)	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma \neq \beta$
Martensite (R)	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

phases, and control of the microstructure [27]. Physical properties of materials are strongly correlated with compositions and phases. Equiatomic NiTi (50 atomic% Ni, 50 atomic% Ti) shape memory alloy is an ordered intermetallic compound [3, 28].

Partial phase diagram of NiTi system is given in Figure 3 [3]. B2 phase region is known to be very narrow at temperature below 923 K. It is generally accepted that B2 phase region is only between 50 and 50.5 atomic% nickel. If nickel content is higher than 50.5 atomic%, then the alloy will decompose during cooling below 973 K to TiNi and TiNi<sub>3</sub>. Ti<sub>3</sub>Ni<sub>4</sub> and Ti<sub>2</sub>Ni<sub>3</sub> are intermediate phases formed during transformation. The central part of Figure 3 where TiNi transforms to monoclinic B19' martensitic phase is important. For the titanium rich side, equilibrium phase is Ti<sub>2</sub>Ni and TiNi [3, 5, 28].

Nitinol based devices have been used in humans since the mid-1970s. Nitinol is now being practically used for various applications, for example, automotive applications, aerospace applications, eyeglasses, window frames, pipe couplings, antennae for cellular phones, actuators, sensors, seismic resistance, damping capacity, shock absorbers, automatic gas line shut-off valves, and SMA spring in water mixers [1, 29–33]. Some researchers are also working to increase the transformation temperatures of NiTi shape memory alloys so that these alloys can be used for high temperature applications. There is a detailed review about high temperature shape memory alloys [34].

If NiTi alloy is constrained to shape change upon phase transformation, then 700 MPa stresses can be generated, which are too much as compared to shape memory polymers where the amount of stress is much smaller. Due to the possibility of large recoverable strain of about 8% without force generation and 700 MPa stress without recoverable strain, there is a high possibility to use NiTi shape memory alloy for the design of components with different strain outputs and different amounts of external work output [3].

## 2. Biomedical Applications of Nitinol

Biomedical applications of nitinol are related to transformation temperatures of nitinol that are close to body temperature (310 K). Due to thermoelastic martensitic phase transformation and reverse transformation to parent austenite upon heating (shape memory effect) or upon unloading (superelasticity), nitinol has a large number of biomedical applications [35, 36]. Another important property of nitinol is its low elastic modulus close to natural bone material

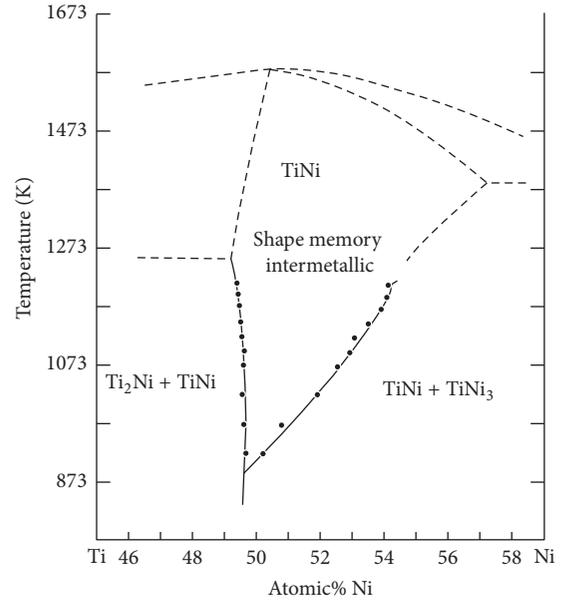


FIGURE 3: Partial phase diagram of NiTi from 45% nickel to 59% nickel. Details of this figure are given in [3].

and compressive strength higher than natural bone material which makes it an ideal material for biomedical implant applications [37, 38]. In the medical field, nitinol has many applications; for example, it can be used as guided wire and heart valve tool, can be used in joining of fractured bones, and can be used as stent, as a guided wire, and as an orthodontic wire or brace [3, 39]. Attachments to each tooth in front of the teeth are called brackets. When NiTi arch wires are attached to brackets, teeth can move in a controlled manner [3]. Pitting corrosion of nitinol is better than SS304 stainless steel in saliva solution [40]. In [41], effects of processing on the properties and biomedical applications of nitinol are discussed. Some of the biomedical applications of nitinol (e.g., orthodontic arch wire, guided wire, bone fixation, and stent) are shown in Figure 4.

*2.1. Applications of Nitinol as Arch Wire.* Nitinol has been used in the dental field as an orthodontic arch wire for more than 20 years. Nitinol uses superelasticity for its use as an arch wire. Nitinol can be used in orthodontics due to its large strain recovery capacity and due to the generation of stresses that are useful for the alignment of teeth in the orthodontic process. NiTi arch wire can generate continuous orthodontic force even with teeth movement as this wire will change its shape during teeth alignment [3]. Nitinol has better pitting resistance when used as orthodontic arch wire in saliva solution as compared to stainless steel [40]. During phase transformation, if shape memory alloys are being stopped to change their shape, then stresses as high as 700 MPa can be generated and these stresses are useful for aligning of teeth. Other applications of nitinol are in dental implants and as attachments for partial dentures where the mechanism of shape memory effect is used [3, 33, 42]. Corrosion resistance of nitinol is significantly lower in fluoridated saliva than in nonfluoridated saliva [40, 43].

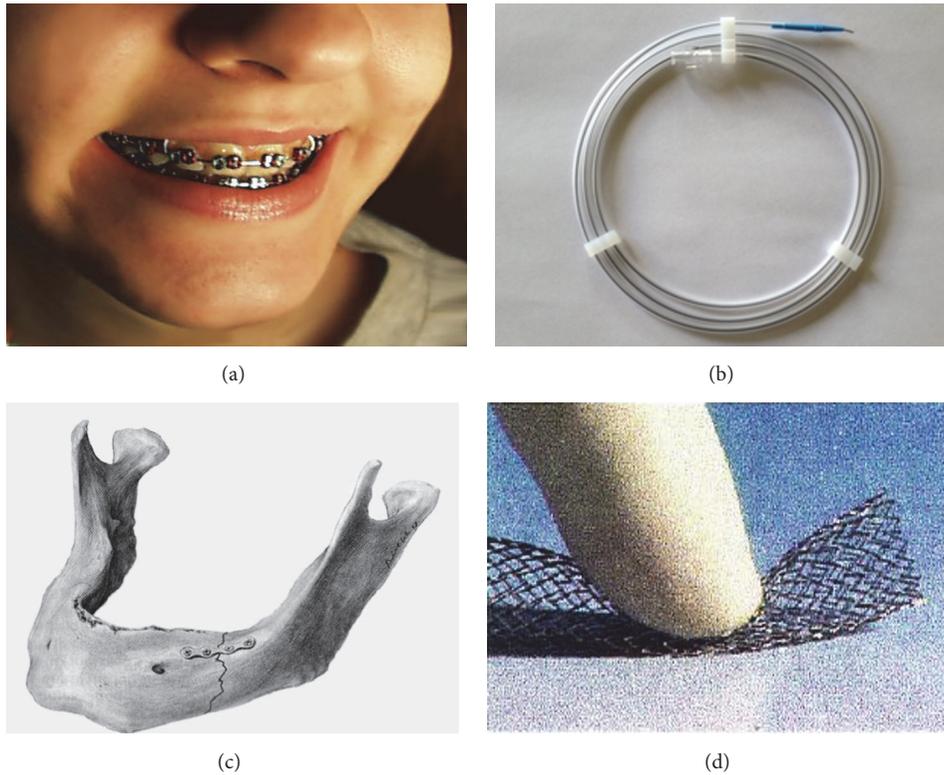


FIGURE 4: Biomedical applications of nitinol. (a) Orthodontic arch wire. (b) Guided wire. (c) Bone fixation. (d) Stent.

**2.2. Comparison of Nitinol with Stainless Steel Arch Wire.** Stainless steel has high elastic modulus as compared to nitinol whose modulus is close to bone material [37, 38]. If stainless steel having high elastic modulus is used as arch wire, then effective strain range related to an optimal force zone will be very small. The nature of applied stress in optimal force zone is such that the teeth alignment will be most efficient and it will support the optimum biological response. Excess force zone exists above the optimal force zone where there is a high possibility of tissue damage. Suboptimal and subthreshold force zones exist below the optimal zone where teeth move less efficiently, and if forces become minimal, then teeth may even come to a complete standstill without any teeth alignment. For nitinol that has low elastic modulus, effective strain range is large with wider optimal force zone. Therefore, nitinol having low elastic modulus provides a greater range of activation and fewer adjustments will be required for arch wire to move the teeth to their final positions. Nitinol arch wires having low elastic modulus have been successfully used as orthodontic wires [3]. Pitting corrosion of nitinol is better than SS304 stainless steel in saliva solution [40, 43]. Comparative studies of properties of different shape memory alloys for actuator applications are given in [44].

**2.3. Applications of Nitinol as Guided Wire and in Endoscopes.** Figure 4 shows some of the biomedical applications of nitinol. Particularly, a biomaterial with low modulus of elasticity is required to be used as a guided wire. Guided wire is a thin metal wire. It is entered through a natural opening or small

incisions. Using NiTi shape memory alloy, nitinol guided wire reduces the chance of injury [3, 45]. One of the most sophisticated medical applications of shape memory alloys is active endoscope. Endoscopes are used in the general areas of the medical industry. A significant improvement was made in the flexibility and control in endoscopes by the use of nitinol shape memory alloy [46–48].

**2.4. Applications of Nitinol in Stent.** Other biomedical applications of nitinol include blood clot filters and stents in cardiovascular treatments. These alloys change their shape upon phase transformation and so they can be used as blood clot filters and as stents in cardiovascular treatments [49–51].

**2.5. Applications of Nitinol in Orthopedics.** A NiTi shape memory alloy is also a good material for use in orthopedic surgery. NiTi shape memory alloys have been used for bone plates to determine and fix fracture spine in scoliosis device (e.g., in higher shoulder) operation. During the transition phase, if the shape memory alloy stops to change its shape, it can generate stresses up to 700 MPa and these stresses are useful to join broken bones. The elastic modulus of NiTi is too close to that of the bone material of the human body and can also be used as an implant [3, 32, 52, 53].

**2.6. Applications of Nitinol in Artificial Organs.** Nitinol has applications in artificial organs, artificial kidney, and artificial heart pump and as actuator in ureteral stenosis after kidney

transplantation [3, 54]. These applications need high fatigue strength and demand for miniaturization; NiTi alloy can meet both needs [55, 56]. NiTi shape memory biomaterials similar to other titanium based shape memory alloys due to thermoelastic martensitic transformation have great recovery strain and better low stress high cycle fatigue life compared to other metallic biomaterials [57]. Micromachines and microrobots require a microactuator. Thin film shape memory alloy is one of the many candidate materials for microactuators [58, 59]. Due to the size effect, slow response of bulk shape memory alloy can be improved by thin film technology.

### 3. Biocompatibility Issues of Nitinol

Nickel is a toxic element and causes contact allergy. In Europe, about 20% of the female population is allergic to the use of nickel. [43]. For good biocompatibility, nitinol should have good corrosion resistance so the release of nickel should be minimum [1, 3, 42]. Different researchers have studied the corrosion behavior of NiTi at body temperature (303 K). Some studies have been carried out in saliva solution [60] and some studies are carried out in Hank's solution [61]. In order to improve the biocompatibility of nitinol, the current author of this study has also studied the effect of partial substitution of nickel with silver on the biocompatibility and corrosion behavior of nitinol in saliva solution and at 303 K [62]. Authors of [63] proposed the artificial saliva after studying the corrosion behavior of different biomaterials in 25 males' and 25 females' saliva solution mixture. The current author also used this composition of artificial saliva solution [63] for in vitro biocompatibility and corrosion behavior of NiTi-Ag intermetallic shape memory material [62]. For orthodontic use, most of the studies used testing solution at pH of 7 (neutral) [40–42]; however, during daily life, pH usually ranges from 4 to 5.5 (acidic), and after a meal it even falls below this value. Corrosion resistance of nitinol decreases significantly with medium acidification. Toothpastes used for the cleaning of teeth contain up to 1% sodium fluoride (NaF) and/or  $\text{Na}_2\text{FPO}_4$ . It is also reported that the corrosion resistance of nitinol significantly reduces in fluoridated saliva solution [43].

The biomaterial, when implanted into the human body or as braces, experiences specific mechanical and electrochemical interactions with the environment. For this reason, biomaterials, for example, stainless steel, Co-Cr alloys, titanium alloys, and nitinol, should have properties to remain stable under such hostile environment [3]. It is reported that titanium and nickel are released from nitinol into the surrounding body environment due to interaction of the biomaterial with the surrounding environment [64]. Potential danger of nitinol is associated with the negative effects of the release of nickel ions into the human body [3, 65]. Nitinol has poor corrosion properties in halide containing environment [43]. Venugopalan and Trépanier [21] reported 13  $\mu\text{g}/\text{day}$  on average nickel ions release from nitinol braces in saliva environment.

Biofilm formation due to interaction of bacteria with the biomaterial affects the biofunctionality of the biomaterial. Biofilm results in some infectious diseases and affects the

implant life. Understanding and control of biofilm formation will improve the implant life and patient health [66]. Biofilm results in oxygen differential cell formation, and acid metabolic products accumulate near the implant surface which results in the acceleration of cathodic reaction. Biofilm contains 75–95% water and the remaining is microorganisms. Biofilms generally decrease the corrosion resistance of implant material and also change the mode of corrosion taking place on the implant surface [67].

Silver is famous for its bacteria killing properties and coatings having silver addition are good against a number of bacteria [68] and there are some reports about NiTi-Ag shape memory alloys [62, 69]. Researchers are working to improve the corrosion and biocompatibility of nitinol by three different ways: (1) addition of a third element in nitinol [34, 62, 69, 70], (2) thin films formation on the surface of nitinol [58, 71], and (3) nickel-free titanium based shape memory alloys [72–74].

Ma and Wu [75] reported that NiTiTa has better corrosion resistance as compared to nitinol. Wen et al. [76] found that partial substitution of Ti with Cu improved the corrosion properties of nitinol. Ag, Nb, Zr, Mo, and Ta are biocompatible and are nontoxic. These elements form a passive oxide layer that hinders the release of nickel into the body environment. Saliva is related to the mouth environment. Duffó and Quezada Castillo proposed a new artificial saliva solution [63]. Duffó and Quezada Castillo in their paper concluded that four different dental alloys tested in their proposed artificial saliva solution showed an electrochemical behavior similar to that obtained in natural saliva. Cioffi et al. [43] carried out an electrochemical release test of nickel-titanium orthodontic wires in artificial saliva and concluded that different phases and temperature influence the nickel release rate trends. The current author's Ph.D. thesis work, completed in 2012 from Hosoda-Inamura Lab, Tokyo Institute of Technology, Japan, was related to nickel-free titanium based shape memory alloys for biomedical applications [77]. The current author has published a number of papers related to nickel-free titanium based shape memory alloys for biomedical and engineering applications in international journals [78–86]. During postdoctoral work from 2012 to 2014 in the High Temperature Materials Unit, National Institute for Materials Science (NIMS), Tsukuba, Japan, the current author's research activities were related to TiPt and TiAu based intermetallics for high temperature applications and he has published papers in international journals [87–94].

*3.1. Biocompatibility Aspects of Thin Films on Nitinol.* Diamond-like carbon (DLC) film is famous for its biocompatibility and resistance to chemicals. DLC film coatings protect the biomaterial from degradation and improve the stability of biomaterials. Further research is in progress related to DLC films on orthodontic devices [71]. Yeung et al. [95] reported the effects of nitrogen plasma implantation on NiTi alloys and reported that TiN layer formed during nitrogen plasma implantation has better wear and corrosion properties. TiN layer also decreases the nickel ions release. Titanium-silver alloys coatings have higher corrosion resistance than pure titanium [96].

#### 4. Nitinol and Stainless Steel as Biomaterial

As opposed to stainless steel and cobalt-chrome wires, nitinol wires, due to their superelastic properties, allow the dentist to apply light and continuous force to teeth, reducing the potential of patient discomfort, tissue hyalinization (i.e., condition of disrepair), and undermining resorption. Hence, the use of NiTi alloy is widespread, especially during the first course of orthodontic treatment, when teeth are strongly misaligned; in these conditions, NiTi is in plateau region (on average 1–8% strain) and releases constant loads [3]. The most recent development in applying shape memory materials for biomedical applications is given in [97].

In short, there are a large number of biomedical applications of nitinol [98, 99] and there is a good book on the biomedical applications of shape memory alloys by Yoneyama and Miyazaki [100]. Professor Miyazaki from the University of Tsukuba and Professor Hideki Hosoda from Tokyo Institute of Technology, Japan, are famous professors in the field of shape memory alloys.

#### 5. Conclusions

Mechanisms of shape memory effect and superelasticity are presented in this paper. An overview of biomedical applications of nitinol and NiTi based shape memory alloys is briefly presented in this paper. Biocompatibility issues of nitinol and researchers approach to overcome this problem are also discussed in this paper. The author's contribution to the field of titanium based shape memory alloy is also briefly presented in this paper.

#### Competing Interests

The author declares that there are no competing interests regarding the publication of this paper.

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