Nickel-titanium based nanocomposites for orthopedic applications: the effects of reinforcements

R. Singh[a,d,*], A. K. Sharma[b], A. K. Sharma[c]

[a]*Research Scholar, Department of Mechanical Engineering, Rajkiya Engineering College, Mainpuri, India*
[b]*Associate Professor, Department of Mechanical Engineering, Rajkiya Engineering College, Mainpuri, India*
[c]*Assistant Professor, Department of Mechanical Engineering, Institute of Engineering and Technology, Lucknow, India*
[d]*Dr. A P J Abdul Kalam Technical University, Lucknow, India*

Owing to better mechanical properties and shape memory effect, the nickel-titanium (NiTi) alloy is a favorable material for orthopedic implants. However, low wear resistance and limited biocompatibility of NiTi can be enhanced by nano-sized reinforcements. Several NiTi-based nanocomposites are developed using nano-sized ceramic reinforcements. Similarly, bioceramic (i.e., HAp) reinforced NiTi nanocomposites are also developed to improve their bioactive properties. However, these nanocomposites show high interconnected pores that severely affect their mechanical strength, corrosion resistance, and biocompatibility. Therefore, some further improvements are required to balance the mechanical and biological properties of NiTi-based nanocomposites. This paper provides a better understanding of NiTi-based nanocomposites developed for orthopedic applications and the resultant effects of nano-sized reinforcements on mechanical, wear, corrosion, biocompatible and bioactive properties. Besides, the synthesis of NiTi nanocomposites using the powder metallurgy process and the effects of process parameters on the nanocomposite properties were also discussed.

1. Introduction

The development of orthopedic implants gained enormous attention in recent years to improving the quality of life. Generally, implants are made of natural or artificial materials to replace the injured or lost structure of human bone. The National Institutes of Health reported that the demand for biomedical implants increases rapidly with increased bone diseases and injuries caused by the world's aging population and lifestyle changes [1]. According to Allied market research [2], the global requirement for medical implants estimated at $77,738 million in 2016, which expect to achieve $124,154 million from 2017 to 2023, with an annual growth rate of 6.9%.

In the past few years, several metals and alloys are developed to fulfill the demand for medical implants in which nickel-titanium (NiTi) alloy attracted much interest due to better mechanical strength and good fatigue life. The NiTi alloy possesses a low young's modulus similar to the human bone that enables the proper distribution of the load at the implant interface and surrounding bone tissues. The bone-like Young's modulus of NiTi offers low stiffness and minimized stress shielding effect [3–5]. Additionally, the NiTi alloy shows some unique properties, such as superelasticity (SE) and shape memory effect (SME) (Table 1), which differentiate these alloys from other titanium (Ti) alloys (e.g., CP-Ti, Ti-6Al-4V, and Ti-Nb-Zr) [6]. Despite these exceptional characteristics, weak osseointegration was observed on the NiTi surface, delaying the therapeutic time and causes the implant loosening. The release of Ni ions is another problem, which triggers toxic and allergic reactions and diminishes the distribution of bone-making cells on the surface of NiTi implants. NiTi alloy also shows a lower compressive

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strength under dynamic loading and lack of wear resistance that can cause premature failure of implants [7–12]. Therefore, it is essential to improve the wear-resistance, osseointegration, and biocompatibility of NiTi-based materials owing to orthopedic applications [13–15].

Table 1. Advantages, limitations and applications of common NiTi alloy used for orthopedic implants.

Alloy	Advantages	Limitations	Applications	Ref.
NiTi	Shape memory and superelastic effects. low stiffness, similar Young's modulus, high mechanical strength	Low corrosion resistance, poor wear resistance, Low biocompatibility and bioactivity	Bone fracture plate, internal fixators for long bone shafts, spinal correctors, vertebral spacers and bone distraction devices	7,9

Recently, many NiTi-based nanocomposites (NCs) are developed that can serve as a suitable material for implant applications. A Nano-sized reinforcement provides a large number of grain boundaries and a high surface-to-volume ratio that offers improved mechanical properties of NiTi implants. Grain refinement mainly depends on the size and concentration of the reinforcement. Similarly, the homogenous dispersion of reinforcement particles provides enhanced microstructure lead to improve the wear and biocompatible properties of NiTi implants [16]. These reinforcements also enhance the physiochemical properties to promote bone integration, adhesion, and proliferation. These NiTi composites reinforced with nano-sized materials play a vital role in enhancing the implant performance because the natural bone is a real nanocomposite [17,18].

This review focused on setting up a significant platform that gives detailed information of essential properties owing to implant applications, NiTi-based NCs developed with different reinforcements and their fabrication process. It unfolds the effect of nano-sized reinforcements and processing parameters on the mechanical and biological properties of NiTi composites. Further, recent issues and challenges of NiTi-based NCs are also described and addressed for this rapidly growing area of research.

Fig. 1. Description of essential properties required for NiTi-based orthopedic implants.

2. Essential properties of NiTi implants

The purpose of orthopedic implants is to regain the structural stability and functioning of injured bones. Generally, implants which can serve safely without any failure should have many essential properties such as low density, high mechanical strength, bone-like Young's modulus,

negligible toxicity and osteoconduction (Fig.1) [19–21]. These essential properties of NiTi-based NCs developed for orthopedic applications are discussed below.

2.1. Mechanical properties

The implants must be able to support body weight during body movement and retain their shape and size under a repeatedly applied mechanical load throughout the patient's life span. The implant material preferably has a similar Young's modulus to the bone. Tensile strength, compressive strength, and toughness are some other important properties that refer to implant materials (Table 2) [22,23]. Abidi et al. [24] fabricated a porous NiTi alloy which shows similar Young's modulus (1.98 GPa) and compressive strength (107 MPa) compared to human bone. Shiva et al. [25] demonstrated that higher Ni content in NiTi enhanced the ultimate tensile strength (296–320 MPa) while higher Ti content leads to improve micro-hardness (380–525 HV) due to the formation of the brittle Ti-rich $NiTi_2$ phase in the structure. However, larger Young's modulus causes stress shielding due to improper stress transfer to the adjacent bone [26,27]. Therefore, a material with high strength and bone-like modulus must be used to minimize the chances of implant loosening and revised surgery.

Table 2. Mechanical properties of NiTi-based implant materials compared with the properties of cortical and cancellous bone [9,10,17,22–24].

Bone/Material	Density $(g.cm^{-3})$	Young's modulus (GPa)	Yield stress (MPa)	Tensile strength (MPa)	Compressive strength (MPa)	Fracture toughness $(Mpa.m^{1/2})$
Bone (Cortical)	1.8–2.0	1–20	30–70	70-150	49–230	2–12
Bone (Cancellous)	0.1–1.0	0.05–0.5	3–5	10–20	15–35	0.1
NiTi	6.6–6.8	80	140	1100	320	30–60

2.2. Shape memory effect and superelasticity

Shape memory is a temperature-induced transformation of material that offers deformation under external force at a certain temperature and gets back to its original shape after heating up to the transformation temperature. Similarly, superelasticity is a stress-induced transformation of material to experience large deformations and immediately return to its original shape after removing force [28]. NiTi alloy is a commonly known material that exhibits shape memory effect (SME) and super-elasticity (SE) due to solid-state thermoelastic transformation [29]. A solid-state phase transformation in NiTi is defined by four transformation temperatures (i.e., martensite start M_s, martensite finish M_f, austenite start A_s, and austenite finish A_f) which was mainly depends on grain size, composition (Ni/Ti content), and sintering conditions of alloy [30,31]. Wen et al. [32] demonstrated the SME of NiTi (Fig. 2). Initially, the NiTi sample was loaded and bent for 180^0 at room temperature (Fig.2a). After unloading, the bending angle of the sample rebounded to 100^0, and the sample was heated to 80 ^{0}C (Fig. 2b). Finally, the sample was returned to its original shape, representing the SME of NiTi (Fig. 2c). The recovery temperature of 80 ^{0}C was opted due to the austenite finish temperature (A_f) of the NiTi sample was 79.1 ^{0}C as shown in Fig. 2d. It observed that the SME and SE degrade by accumulated residual strain caused by dislocation slipping at the austenite-martensite interfaces [33] and residual martensite phase due to incomplete reverse transformation [34]. This unwanted phenomenon depends on precipitated phases and heat treatment parameters (e.g., solution annealing temperature and time, quenching, and aging temperature and time) [35,36]. Tang et al. [37] reported that the austenite-martensite transformation increases with higher sintering temperature, which results in lower residual strains. The results demonstrated that the residual strain increases due to microstructural defects, retained martensitic phase, and resultant plastic deformation.
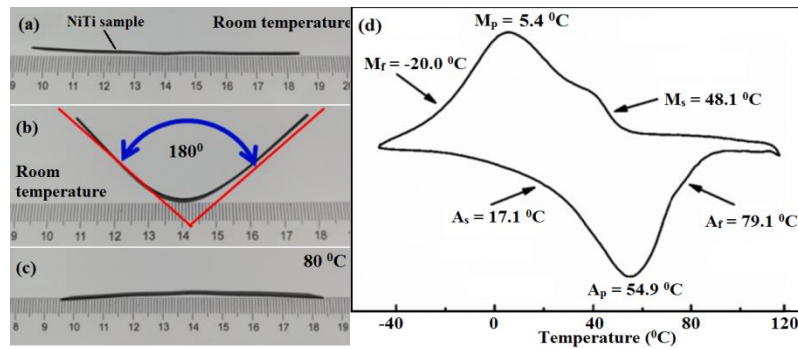
Fig. 2. (a) NiTi sample at room temperature, (b) NiTi sample after loading at 180^0, (c) NiTi sample after heated at 80 ^0C showing Shape memory effect and (d) transformation temperatures of NiTi alloy (reproduced with permission from [32]).

2.3. Wear properties

Low wear resistance can cause a subsequent release of metal ions from the adjacent surfaces of the implant (e.g., hip, shoulder, knee, and elbow joints) due to relative movement under dynamic loading. Such particles can lead to adverse allergic and toxic effects on the human body [38,39]. Ng et al. [40] and Zhao et al. [41] show that the NiTi has higher surface wear due to the release of micro-level Ni particles during the movement of implanted joints. This unusual mechanical degradation of Ni ions causes adverse effects (e.g., toxicity, allergies, and carcinogenic effects) and restricts the long-term applications of NiTi implants. Similarly, aseptic loosening is another problem caused by wear due to the accumulation of fine particles on the bearing surfaces of the implant. The increased wear particles can activate immune system macrophages that identify and absorb these foreign particles, similar to bacteria or pyrogens. However, foreign particles tend to damage macrophages after ingestion, releasing enzymes and metabolites in the surrounding environment that cause severe acidification. These acidic chemicals and wear particles lead to implant erosion which promotes premature implant failure and the requirement of revision surgery [42,43].

Table 3. Important factors influencing the corrosion of implants (reproduced with permission from [44,45]).

Corrosion of metallic implants	Presence of chloride and other ions
	Presence of bio-molecules and proteins
	pH and dissolved oxygen
	Alloying elements
	Surface topology
	Implant design

2.4. Biostability

The biostability of an implant refers to its long-term success in the physiochemical environment of the human body. It is susceptible to corrosion and oxidation due to chemical reactions on the implant surface when it comes into contact with body fluids. The corrosion behavior of the implant is affected by a wide range of factors (Table 3), including the implant material and its surrounding environment [44,45]. Talha et al. [46] observed that the proteins could lead to corrosion by sticking with metal ions and move them away from the implant surface that

minimizes the absorption of oxygen. Similarly, the aqueous ions, such as chloride (Cl^-), promote corrosion in ambient conditions [47]. In orthopedic implants, increased corrosion can minimize the implants' structural strength, leading to subsequent failure of implants [48]. On the other side, oxidation of NiTi alloy develops a surface layer of titanium oxide, which is highly stable, and its neutral behavior in a corrosive medium provides excellent corrosion resistance [49−51].

2.5. Biocompatibility

The corrosion resistance and formation of the oxide layer are the main factors that affect the biocompatibility of NiTi, while these factors are not sufficient for excellent biocompatibility (Fig. 3) [52]. The material's biocompatibility is also constrained by reactions between the implant material and the host environment, such as molecular and protein adsorption, cell and bacterial adhesion, tissue development, inflammation, and degradation of implant material [53,54]. Meanwhile, particles produced by wear and corrosion from implants are foreign bodies, which induce subsequent inflammation at the bone-implant interface [55,56]. These foreign bodies can lead to failure of orthopedic implants due to aseptic osteolysis and implant loosening. Hence, non-toxic alloying elements should opt for the design and development of orthopedic implant materials which can serve without irritant or allergic effects in the human body [57].
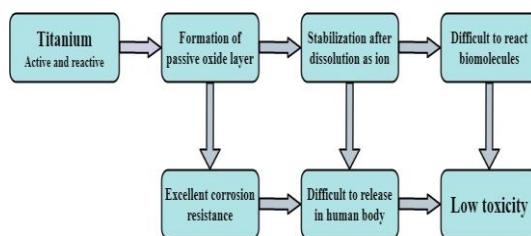

Fig. 3. Evaluation of low toxicity (excellent biocompatibility) governing by corrosion resistance and formation of oxide layer (reproduced with permission from [52])

2.6. Osseointegration

It referred to the implant's ability that provides a structural and functional linkage between the implant surface and bone tissues [58]. Hench & Jones [59] defined that osseointegration is a combination of osteoinductivity and osteoconductivity. Osteoinductivity is a property of implant material by which the new bone tissues are developed on the implant surface and instantly binds to living bone cells. In the same way, osteoconductivity provides suitable bonding between implant with hard tissue. However, improper osseointegration can avoid the development of fibrous tissues and cause implant failure. Factors such as design, alloying elements, surface chemistry, surface finish, and loading conditions are crucial for the proper osseointegration of implants [60,61].

3. Fabrication of NiTi-based NCs

In recent years, researchers focused on using the powder metallurgy (PM) process to fabricate NiTi-based NCs due to ease of processing and no need for post-machining [62]. NiTi NCs fabricated by the PM process show enhanced physical and mechanical properties due to the finer and homogeneous microstructure [63,64]. Besides, composites and near-net-shape parts could also be manufactured using this technique. In this technique, metallic or ceramic powders are mixed and converted to the desired shape by applying pressure and temperature. The matrix material is generally mixed with reinforcement particles and compressed at high pressure in a closed die to form a green compact. Finally, sintering is performed at a specific temperature in a controlled atmosphere to avoid oxidation (Fig. 4) [65,66]. Sintering is an important step in the PM process and responsible for triggering atomic diffusion, which results in strong mechanical integrity and minimum porosity within the composite structure. There are primarily three sintering

methods (e.g., vacuum sintering, spark plasma sintering, and microwave sintering) used to fabricate NiTi-based NCs [67–69].
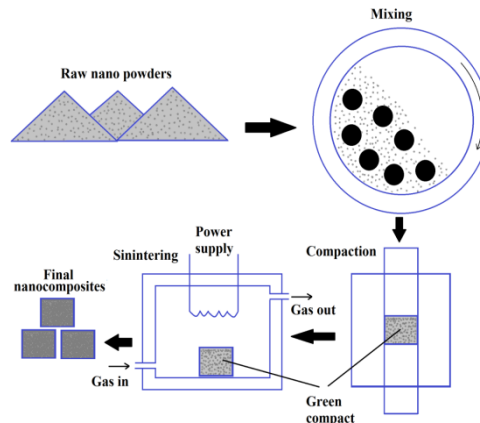

Fig. 4. Fabrication of NiTi nanocomposites using three step (i.e., mixing, pressure compaction and sintering) powder metallurgy process.

Table 4. Advantages and limitations of different sintering methods used in powder metallurgy process.

Method	Advantages	Limitations	Ref.
Vacuum sintering	Lower cost and available for large variety of materials	Formation of undesirable and secondary phases, long time required, and unable to pore control	64
Spark plasma sintering	Low sintering temperature with higher heating rates, short processing time, uniform sintering, avoiding any undesired reaction products and high consolidation	Not suitable for complex, parts, expensive tooling and processing	64, 70, 72
Microwave sintering	Low sintering temperature, enhanced diffusion process, fast heating rates, time and energy saving, Simplicity, Low environmental hazards, uniform porosity, improved mechanical and physical properties	----	68, 73, 74

Vacuum sintering is the conventional method of sintering based on the atomic diffusion of the green compact near the melting temperature. Despite the simplicity and lower cost, the limitations (Table 4), such as the formation of undesirable secondary phases and the requirement of long sintering time, restricted the use of this method to some extent [70–72]. In spark plasma sintering, DC electrical pulse current and uniaxial pressure are used to consolidate powders. Simultaneous pressure provides an additional driving force that result in high densification and grain growth at low sintering temperatures and time [73,74]. Velmurugan et al. [75] used spark plasma sintering to fabricate a dense NiTi composite at 900 ^{0}C with 50 ^{0}C.min^{-1} heating rate. The diffusion of Ni and Ti occurred at low temperatures, and rapid heating rate influenced the plastic

deformation of Ni and Ti particles that causes dense (98%) structure. In recent years, microwave sintering is attracted huge interest for the fabrication of NiTi NCs. In this process, the electromagnetic energy is converted into thermal energy that provides the necessary heat for the sintering of compacts. The main benefits of this method are reduced processing time/temperature, less energy required, and enhanced diffusion that provides finer microstructures results in improved mechanical properties [76].

In powder metallurgy, several process parameters directly influence the final features of NiTi composites. To achieve the desired properties, optimization of these parameters is necessary. Table 5 provides an overview of the most influential parameters of the powder metallurgy technique. The purity, size, and morphology of the primary powders are the most critical factors influencing the final properties of the NiTi composite. It was observed that the higher amount of impurities in Ti powders accelerates the rates of reactions, and a large number of undesirable phases (e.g., Ni_3Ti and Ti_2Ni) were formed during sintering [77,78]. Novak et al. [79] showed that the coarse Ni and Ti particles promote unreacted Ni/Ti areas during sintering. It also reported that an increase of Ni powder size causes large porosity due to more remained β-Ti at 980 ^{0}C. Similarly, non-uniform spherical-shaped particles provide enhanced bonding between the composite particles lead to high density and mechanical strength. The compositional variation of Ni and Ti powders directly affects the transformation temperatures, microstructure, and mechanical properties of the final composite. The increase of Ni content decreases the Ms temperature, while an increase of Ti content enhances the hardness of the composite [7,80,81]. It was observed that the compaction pressure has a direct impact on the product porosity [82]. Similarly, sintering parameters (e.g., sintering environment, sintering temperature, and time) significantly influence the phase evolution, pore characteristics, and mechanical properties. Higher sintering temperature and time both decrease the content of undesirable phases in the final NiTi structure [83].

Table 5. Process parameters and their effects on properties of NiTi nanocomposites [64, 68–70, 75, 76].

Parameters	Effects
Powder purity	Contamination of oxygen, carbon with Ti and formation of undesired $Ti_4Ni_2O_x$, TiO_2, and TiC precipitates
NiTi particle size	Course particle size leads to the formation of un-reacted Ni/Ti areas during sintering and development of high porosity
Powder shape	Inhomogeneous pores distribution causes loss of mechanical strength
Composition	High Ni content results in lower Ms temperature and high Ti content leads to high micro-hardness due to the formation of the brittle Ti_2Ni phase
Compaction pressure	Low compaction pressure increases the composite porosity
Sintering temperature/time	Direct influence on phase evolution, pore size, pore shape, and mechanical properties

NiTi nanocomposites	Ceramic reinforcement	NiTi/Al$_2$O$_3$
	Bioceramic reinforcement	NiTi/HAp
	Nanocomposite coatings on NiTi surface	Au/CS
		TiN
		HAp
		HAp/Si
		HAp/Si/MWCNT
		HAp/ZnO
		HAp/Ta$_2$O$_5$

Fig. 5. Brief classification of NiTi-based nanocomposites developed for orthopedic applications.

4. Nickel-Titanium (NiTi) based NCs

In order to achieve suitable properties, several NiTi-based NCs are developed using several nano-sized reinforcements (Fig. 5). It observed that several nano-sized ceramics such as Al$_2$O$_3$ and ZrO$_2$ are used to develop NiTi NCs. These NCs shows enhance mechanical and tribological properties. Farvizi et al. [84] developed a NiTi nanocomposite reinforced with Al$_2$O$_3$. Similarly, Şahin et al. [85] used Al$_2$O$_3$ nanopowder to synthesize NiTi/Al$_2$O$_3$NCs. Many researchers used nano-sized bioceramic (i.e., HAp) to develop NiTi/HAp NCs, which show enhanced cell viability, adhesion, proliferation, and osteogenesis function. Zhang et al. [86] synthesized a NiTi composite reinforced with nano-sized HAp. In another study, Zhang et al. [87] fabricated a functional structure NiTi/HAp composite. The composite consists of a central NiTi core with 13% porosity and an external porous NiTi/HAp nanocomposite layer with 49% porosity, as shown in Fig. 6a and b. In another study, several nanocomposite coatings are also developed using many other nano-sized reinforcements (e.g., Si, MWCNT, ZnO, and Ta$_2$O$_5$), which enhances the surface properties of NiTi composites.
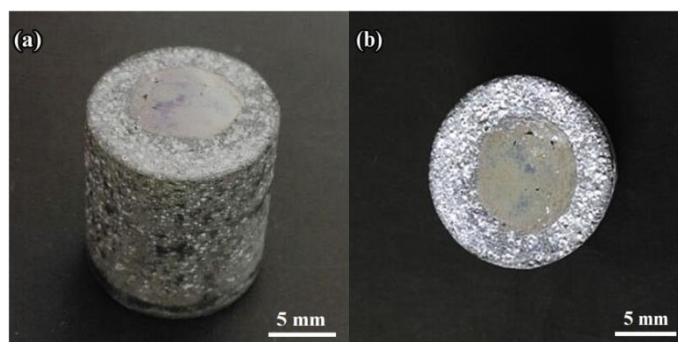

Fig. 6. NiTi/HAp nanocomposite sample with (a) front view and (b) top view which consists of a central NiTi core and an exterior porous composite NiTi/HAp layer (reproduced with permission from [87]).

5. Enhanced properties of NiTi NCs

It observed that the addition of nano-sized ceramics enhances the mechanical and tribological features of NiTi alloy. Similarly, the NiTi composite reinforced with nano-sized HAp produces more stable calcium phosphate phases that enhance the in-vitro bioactivity of NiTi implants. Therefore, several nano-sized reinforcements (e.g., Si, MWCNT, Al$_2$O$_3$, ZrO$_2$, ZnO, and Ta$_2$O$_5$) are used to develop NiTi NCs. The NiTi NCs showed enhanced mechanical, wear, corrosion, and biological properties. These improved properties are the resultant effect of nano-sized reinforcements, which are discussed below.
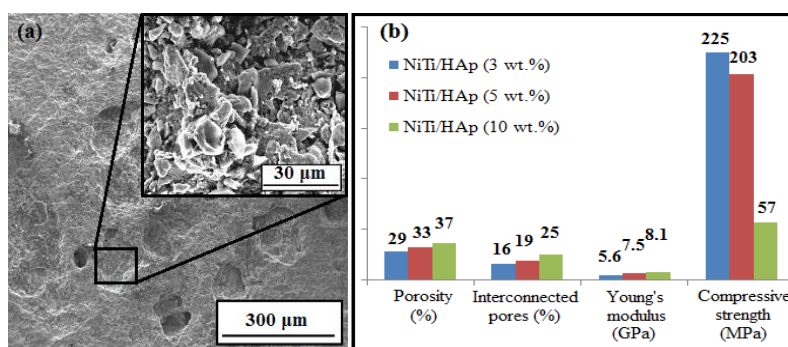
Fig. 7. SEM images of NiTi/HAp nanocomposite sample showing (a) porous surface with magnified view of the region enclosed by black square shows pores interconnectivity, (b) porosity, interconnected pores, Young's modulus and compressive strength of NiTi/HAp nanocomposites (reproduced with permission from [86]).

5.1. Mechanical properties, SME and superelasticity

Zhang et al. [86] show that Young's modulus of NiTi/HAp NCs ranged from 5.6 to 8.1 GPa that significantly matched with Young's modulus of human bones (3−20 GPa for cortical bone). The NiTi/HAp composite (with 3 wt.% of HAp) shows the compressive strength of 225 MPa close to the compressive strength of human bones (100−230 MPa for cortical bone). However, the compressive strength of NiTi/HAp NCs decreased from 225 to 57 MPa due to increase of HAp content from 3 to 10 wt.%, respectively. The high HAp reinforcement produces large pores with significant interconnectivity as shown in Fig. 7a. The high porosity and large interconnected pores increase the Young's modulus of NiTi/HAp NCs. However, it decreases the compressive strength of NiTi/HAp NCs (Fig. 7b). In another study, the functional structured NiTi/HAp nanocomposite shows improved compressive strength (up to 1300 MPa) and Young's modulus (7.9 GPa) [87]. Akmal et al. [88] identified an improvement of 98.7 % in the hardness of NiTi/HAp NCs due to the excellent dispersion of HAp particles. The XRD spectra of NiTi/HAp NCs reveal $NiTi_2$, Ni_3Ti, and Ni_4Ti_3 phases in the composite matrix (Fig. 8) which also influences the hardness of the composite.
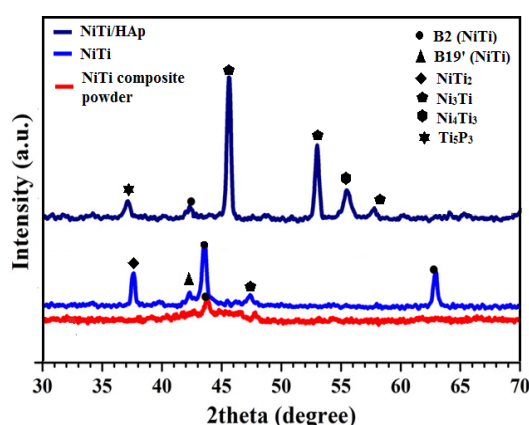

Fig. 8. X-Ray diffraction patterns for ball-milled NiTi powder, NiTi and NiTi/HAp composite after sintering showing developed phases (reproduced with permission from [88]).

The SME and superelasticity of NiTi composites are correlated with the phase transformation temperatures. For example, NiTi composites show a martensitic transformation from high-temperature B2 phase to low-temperature B19′ phase [7]. Similarly, the superelastic behavior of NiTi is utilized where austenite is present at body temperature (i.e., 37^0C) and

transforms to martensite under the application of stress [89]. However, these transformation temperatures depend on the chemical composition, heat treatment, and synthesis processes [90]. Therefore, it is essential to maintain the optimum composition of NiTi NCs to achieve suitable transformation temperatures. Zhang et al. [87] reported a superelastic recovery strain (above 4%) of NiTi/HAp composite up to 22 loading-unloading cycles before failure. A closed-loop stress-strain curve was observed, which indicates a complete superelasticity of the nanocomposite. Farvizi et al. [91] demonstrated the phase transformation behavior of $NiTi/Al_2O_3$ nanocomposite. It observed that the transformation temperatures of $NiTi/Al_2O_3$ nanocomposite were higher than the pure NiTi (Table 6) due to the formation of secondary phases (e.g., $NiTi_2$ and Ni_3Ti) and the presence of Al_2O_3 particles. Akmal et al. [88] showed the transformation behavior of NiTi/HAp composites which range from -33 to 200 ^{0}C. However, no peaks of martensitic transformation were observed due to the formation of secondary precipitates (i.e., $NiTi_2$, Ni_3Ti, and Ni_4Ti_3) in the composites.

Table 6. Phase transformation temperatures of pure NiTi and NiTi/Al$_2$O$_3$ nanocomposite (reproduced with permission from [91]).

Materials	M_s (^{0}C)	M_f (^{0}C)	A_s (^{0}C)	A_f (^{0}C)
Pure NiTi	10	-11	-8	26
NiTi/Al$_2$O$_3$	48	20	59	76

5.2. Wear resistance

Liu et al. [92] observed that the nanoscale reduction of grain size significantly increases the hardness of NiTi alloy and thus directly affects the wear behavior of the composites. The wear resistance of the implant can also be enhanced by surface modification of NiTi. Ng et al. [40] show that the high surface wear of polished NiTi surface reduced to 43.51% by forming a surface coating of titanium nitride (TiN). Similarly, Zhao et al. [41] reported that the Hf implanted NiTi samples show improved wear resistance due to the formation of HfO_2/TiO_2 nano-layer on the NiTi substrate. Therefore, the results reveal that the wear resistance of the modified NiTi surface was far better than the bare NiTi surface. Further, Farvizi et al. [84] evaluated the wear behavior of NiTi alloy reinforced with nano alumina (Al_2O_3). The result reveals that the addition of nano-Al_2O_3 to the NiTi matrix improves the friction coefficient from 0.2 to 0.6 compared to NiTi alloy. The width of the wear track was found approx. 207 μm for $NiTi/Al_2O_3$ nanocomposite and 1211 μm for NiTi alloy indicate that the wear rate significantly reduced after nano-Al_2O_3 reinforcement. Sahin and Öksüz [85] also reported similar wear behavior of $NiTi/Al_2O_3$ nanocomposite due to prevention of dislocation motion in NiTi matrix through a dispersion-strengthening mechanism promoted by strengthening of nano-sized Al_2O_3.

5.3. Corrosion resistance

The fine grain size and nano-sized reinforcements possibly prevent the implant surface from corrosion. Several studies show that the reinforcement of HAp enhances the corrosion resistance of the NiTi alloy and provides a strong barrier for the removal of metal ions due to the accumulation of calcium phosphate coating on the NiTi substrate [93,94]. Zhang et al. [86] revealed the increased corrosion resistance of the NiTi/HAp nanocomposite (36.47 μA.cm^{-2}, −766 mV) compared to NiTi alloy (366.1 μA.cm^{-2}, –1451 mV) However, the corrosion resistance of the NiTi/HAp nanocomposite (182.9 μA.cm^{-2}, −993 mV) was decreased with high HAp contents (10 wt.%). High HAp content increases the porosity of the nanocomposite, which provides a large contact area between body fluid and implant surface. Khalili et al. [95] also observed similar corrosion behavior for HAp coated NiTi alloy. On the other side, HAp/Si (20 wt.%) and HAp/Si (20 wt.%)/MWCNT (1 wt.%) coatings significantly improve the corrosion resistance of NiTi alloy. Sabzi et al. [96] show that the HAp/ZnO nanocoating enhances the corrosion resistance of NiTi substrate. The corrosion behavior of HAp/ZnO coated NiTi alloy and uncoated NiTi alloy was

observed by SEM images (Fig. 9). A protective layer is observed on the HAp/ZnO-coated surface, minimizing material degradation from the alloy surface (Fig. 9b). The images show that the presence of a protective layer minimizes the corrosion attack by reducing the anodic reactions in the simulated environment and change the corrosion mechanism from uniform to localized state. However, no passive layer is formed on the uncoated surface that causes high and uniform corrosion throughout the surface, as shown in Fig. 9a. Thus HAp/ZnO nanocoating develops a protective barrier that reduces the degradation of Ni and Ti ions from the implant surface lead to the improved corrosion resistance of NiTi alloy. Hence, the secondary reinforcements such as Si [95], MWCNT [95], ZnO [96], Al_2O_3 [97], and bioglass [98] with HAp create a dense microstructure which improves the corrosion resistance by minimizing the open contact area between corrosive agents and NiTi substrate.
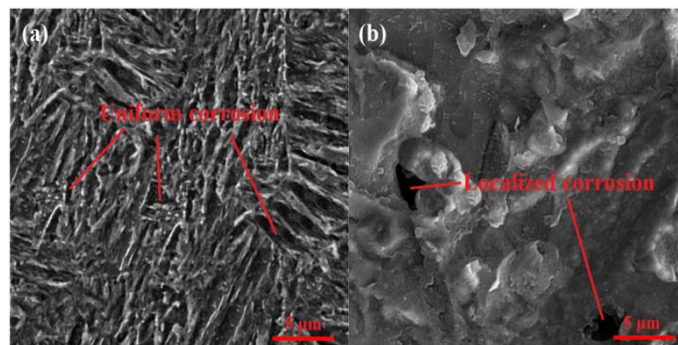

Fig. 9. SEM images of(a) uncoated NiTi alloy showing uniform corrosion and (a) HAp/ZnO coated NiTi alloy showing localized corrosion after a potentiodynamic polarization test (reproduced with permission from [96]).

5.4. Biocompatibility and osseointegration

The removal of Ni ions from NiTi alloy is a major problem leading to toxicity, carcinogen and immune-sensitizing issues [8]. Therefore, it is necessary to improve the surface properties of NiTi alloy to improve its biocompatibility and also to mitigate the removal of Ni ions. Zhang et al. [99] have developed graphene coated NiTi alloy that shows Ni ions released from the coated NiTi alloy is only 46 $\mu g.L^{-1}$ that significantly lower to uncoated NiTi (134 $\mu g.L^{-1}$).The surface modification of NiTi alloy with HAp bioceramic shows a relatively decreased release of Ni ions. However, with higher HAp content, the removal of Ni ions has increased due to induced open porosity [86]. Further secondary reinforcement such as ZnO [96] and Al_2O_3 [97] were used with HAp to develop surface coatings that minimize the removal of Ni ions from NiTi substrate. Recently, Horandghadim et al. [100] fabricated the HAp/Ta_2O_5 nanocomposite coating on NiTi substrate. It observed that the increased reinforcement of Ta_2O_5 (20 wt.%) with HAp on the NiTi surface subsequently minimizes the removal of Ni ions (5.62 $mg.L^{-1}.cm^2$) compared to the Hap coated NiTi alloy (45.72 $mg.L^{-1}.cm^2$). Such a phenomenon can be attributed to the reduction of open porosity by secondary reinforcement of Ta_2O_5, which restricts the flow of phosphate-buffered saline (PBS) solution through the pores and ultimately reduces the release of Ni ions. Ahmed et al. [101] have analyzed the antibacterial behavior of Au/CS coated NiTi against bacteria S. aureus. The 100% antibacterial rate with negligible CFUs of S.aureus was identified on Au/CS coated NiTi, showing higher growth prevention for standard bacteria than uncoated NiTi.

It was observed that the oxide layer formed on the NiTi surface can reduces the bioactivity due to reduced cell adhesion and proliferation [102]. Jin et al. [103] show the results of L-929 murine fibroblast cells cultured on the TiN-coated NiTi and uncoated NiTi alloy. The cells are uniformly attached and proliferated in a large quantity on TiN-coated NiTi surface compared to uncoated NiTi surface. It represents enhanced proliferation and fibroblast adherence due to increased roughness and wettability. Zhang et al. [87] also analyzed the cell behavior of NiTi/HAp NCs against ROS1728 cells. The cells were uniformly distributed around the nanocomposite

surface and growing into pores, which revealed improved cell adhesion and proliferation without any inversive reactions of ROS1728 osteoblasts on the nanocomposite surface. Zhang et al. [86] immersed the samples in SBF for identifying osseointegration of NiTi/HAp NCs. Fig.10a shows the SEM micrographs of porous NiTi composite without HAp, revealing a few apatite particles accumulated on the pore walls. However, a homogeneous calcium-phosphate (Ca–P) layer with plate-like crystal was seen on the surface of NiTi/HAp nanocomposite (Fig. 10b). The results show that the bone-like calcium phosphate film is developed on the nanocomposite surface. Moreover, many nucleated particles of calcium phosphate fill the open pores and develop a homogenous bioactive layer throughout the composite. Several studies reported that the thickness and homogeneity of the apatite layer greatly enhanced with an increase of HAp content. In the meantime, integrated open pores lead to the free flow of body fluid and nutrient solution that provide vast space to promote osteoblast formation [86,104,105].
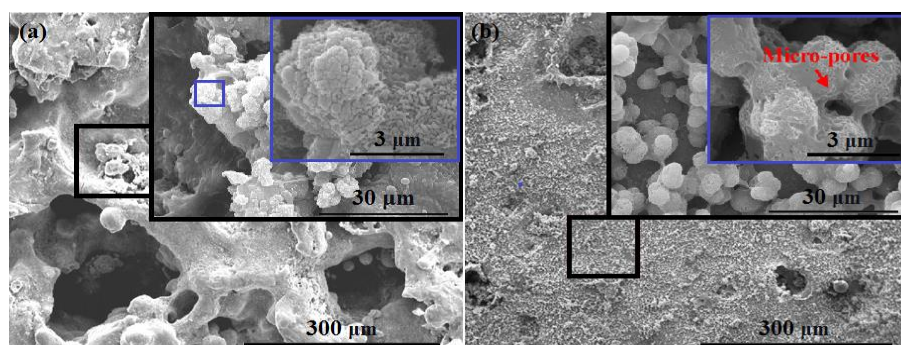

Fig. 10. SEM micrographs of (a) porous NiTi composite without HAp and (b) NiTi/HAp nanocomposite with 3 wt.% of HAp showing apatite formation (reproduced with permission from [86]).

6. Summery

The bone-like properties of implant material are an essential aspect of the safe and long-term functioning of orthopedic implants. These properties are influenced by alloying chemistry and metallurgical physics that can be improved by reinforcing nano-sized materials [9,10,16]. Several NiTi-based NCs are developed for implant applications which show improved mechanical strength and corrosion resistance compared to conventional metal implants [17,18]. However, several issues were also identified with these NCs, such as low mechanical strength, high corrosion, and release of toxic elements. In order to understand these issues, a summary matrix was prepared for NiTi-based NCs with different reinforcements (Table 7), where "Y" indicates that the issues are addressed or resolved.

Many studies reported that the NiTi alloys are reinforced by several nano-ceramics such as Al_2O_3 [84,85], ZrO_2 [93], ZnO [96], and Ta_2O_5 [101,105]. NiTi-based NCs developed with these hard ceramics show improved hardness and wear resistance due to the development of hard phases and a passive layer on the nanocomposite surface (Table 8). The formation of a passive layer also helps to improve the corrosion resistance and subsequently biocompatibility by minimizing the release of unwanted metallic ions. However, the brittle nature of these ceramics causes higher young's modulus and lower compressive strength. The low bioactivity is another major factor caused by the formation of the passive film, which prevents osteoblast formation and osseointegration on NCs surface. Therefore, the researchers introduced a bioceramic material (i.e., HAp) which is chemically similar to the bone and helps to improve the biological properties of NiTi NCs. The NiTi/HAp NCs [86,87] show enhanced hardness and wear characteristics as this bioceramic is also known as a white lubricant. On the other side, the strengthening of nano-sized HAp demonstrated enhanced bioactive behavior due to developed calcium phosphate layer on the NCs surface. The NCs reinforced by HAp show interconnected porous structures that stimulate the free flow of body fluid, leading to sufficient osteoblast formation. However, a high content of bioceramic deteriorates the mechanical strength of developed NCs due to high porosity. It also

creates larger open pores that provide large surface contact of the implant with the corrosive agents leading to high corrosion and release of unwanted elements.

Table 7. Summary matrix of NiTi-based NCs with reinforcements where "Y" indicates that the issues are discussed or resolved.

NCs	Reinforcement/ coating	Young's Modulus	Mechanical strength	Hardness	Wear resistance	Corrosion resistance	Biocompat- ibility	Bioactivity	Ref.
NiTi based NCs	Al_2O_3	Y		Y	Y	Y			84, 85
	HAp	Y	Y	Y	Y	Y	Y	Y	86–88
	HAP/ZrO_2					Y	Y	Y	93, 97
	HAp/ZnO					Y		Y	96
	HAp/Ta_2O_5	Y		Y		Y	Y	Y	100, 105
	Au/CS						Y	Y	101

Table 8. Effect of reinforcements on the properties of NiTi based NCs for orthopedic implants.

Reinforcements	Material	Positive effect	Negative effect	Ref.
Ceramic	Al_2O_3	Improved hardness, wear-resistance, corrosion resistance and biocompatibility with minimum release of unwanted metallic ions	Higher young's modulus, lower compressive strength, lack of SME, lower osteoblast formation and osseointegration	84, 85
	ZrO_2			93, 97
	ZnO			96
	Ta_2O_5			100, 105
Bioceramic	HAp	Similar Young's modulus, enhanced hardness, wear characteristics and bioactivity	Lower mechanical strength, higher corrosion and release of unwanted metallic ions	86–88

Several nanocomposite coatings were also developed with HAp to improve the surface properties of NiTi-based implants, but these nanocoatings reveal similar behavior compared to NiTi NCs developed with bioceramics. So, to match the mechanical and biological compatibility of the implant surface, several studies reported the use of secondary reinforcements (e.g., Ag, Au, CS, ZrO_2, TiN, and Ta_2O_5) with bioceramic (i.e., HAp) to develop nanocomposite coating on NiTi substrates such as HAp/Ta_2O_5 on NiTi [101,105]. It is observed that the nanocoating developed by secondary reinforcement and HAp greatly enhance the corrosion resistance and cell behavior. It also minimizes the release of toxic ions from the nanocomposite surface with maintaining good surface hardness and adhesion strength. In the similar way, the secondary reinforcements can be used with bioceramic to balance the mechanical and biological properties of NiTi-based NCs. However, no work was found that reports the use of secondary reinforcements with bioceramic to develop structural NiTi NCs.

7. Conclusions

Recent developments in the field of NiTi-based NCs used for orthopedic implants, along with their properties and processing technique, are discussed in this review. The review shows that the process parameters (e.g., compaction pressure, sintering time, and temperature) and nano-sized reinforcement affects the mechanical, tribological, and biocompatible properties of NiTi-based implants. It is observed that the NiTi-based NCs developed with bioceramic (HAp) achieve favorable osseointegration and osteoblast formation. The bioceramic reinforcement also exhibits higher hardness due to better bonding and adhesion between the reinforcement particles and the metal matrix. It provides an interconnected open channel for the free flow of body fluid and nutrient solution, promoting bioactive calcium phosphate layer formation, cell adhesion, and proliferation. However, higher porosity is induced due to high bioceramic content that degrades the mechanical strength of implants. The more significant open porosity provides the wide exposed contact area between the corrosive atmosphere and implant surface, leading to the removal of metallic ions, which negatively affect the corrosion resistance and biocompatibility of the implant materials.

Several nanocomposite coatings were developed by combining secondary reinforcements (Si, Au, ZrO_2, ZnO, and Ta_2O_5) and bioceramic to improve the surface properties of the implant. However, no study has reported in which secondary reinforcement was used to fabricate NiTi-based NCs that successfully balance the mechanical and biological properties of not only the surface but the whole structure of implants. Hence, a secondary reinforcement is also required with bioceramic that provides superior structural homogeneity to better match the mechanical and biological properties of NiTi NCs. In general, the selection of optimal reinforcement and process parameters helps to enhance the mechanical as well as the biological properties of NiTi-based NCs. Such NCs can be successfully used as implant materials to improve the long-term success rate of orthopedic implants.

Acknowledgements

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