

## Niti And Newer Nickel Free Super-Elastic Arch Wires

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**Abstract:** NiTi is one of the most popular alloys in the medical world today, owing to its shape memory, super-elasticity and low elastic modulus. It has its niche in the field of Orthodontics as well, due to the ability of the alloy to deliver light continuous forces, which is biologically and physiologically optimal to effect tooth movement without any detrimental effects on the periodontium. Due to the concerns around Ni hypersensitivity, in NiTi which has 55% Ni, and hence, the potential for causing the plethora of allergic reactions associated with Ni<sup>2+</sup> ion release, various alternative Nickel free alloys have been developed, primarily those in combination with  $\beta$  Titanium. More recently, Shape memory polymers are also being studied (SMPUs- Shape Memory Poly Urethanes). These alloys and polymers have the potential to combine the advantage of shape memory and super-elasticity and completely circumventing the possibility of Ni based allergies because these archwires are practically Ni free. There is still a lack of clinical evidence and most of the studies are carried out *in vitro* or in animals, but they are significant nonetheless.

**Keywords:** NiTi, Superelasticity, Shape Memory, Ti based alloys, Shape memory Polyurethane (SMPU), Ni allergy

### INTRODUCTION

Nickel Titanium has almost been analogous with the terms superelasticity and shape memory, atleast with respect to practical biomedical applications. It has come a long way, since its inception and first commercially available form – *nitinol*, by William F. Buehler and his associates, the name being an acronym for the Nickel Titanium Naval Ordnance Laboratory, in Silver Springs, Maryland, originally made for use in space research in the 1960s.<sup>1</sup> It was then popularized by Andreasen as an effective orthodontic archwire, in the year 1971<sup>2</sup> Over the years various new modifications were made to NiTi<sup>3,4,5</sup> Though various physical and mechanical properties of NiTi have been extensively investigated<sup>3-8</sup>, those that are of the most importance are the super-elasticity and shape memory<sup>9-14</sup>. With NiTi, it is possible to deliver light continuous forces which is physiologically optimal as it prevents hyalinization of the periodontal ligament but at the same time, ensures bone remodeling at an optimal pace for efficient tooth movement, especially useful in the initial levelling and alignment phases.<sup>15</sup> Due to the high Nickel content in Ni based alloys like NiTi (55%) and the long duration of contact in Orthodontic treatment, there is some concern about the biocompatibility of the alloy. Though it is usually well tolerated, it potentially puts the patients at the risk of Nickel hypersensitivity<sup>16</sup> and contact dermatitis<sup>17</sup>. 40-70% of patients with contact dermatitis can develop hand eczema which may be acute or chronic. This is caused mainly due to the Ni<sup>2+</sup> ion release. This ion release is also influenced by the surface defects that increase Ni<sup>2+</sup> ion release due to corrosion.<sup>18</sup> Due to the concern about the biocompatibility of Ni based alloys, Ni free shape memory and superelastic alloys are being developed studied in recent times. Cu-Zn-Al and Cu-Al-Ni were studied for their good properties and low cost but Cu, Ni, and Al, aren't too great on the biocompatibility front.<sup>19</sup>  $\beta$  titanium alloys offer low elastic modulus, greater ductility, corrosion resistance<sup>20,21</sup> when compared with alloys that are a combination of  $\alpha+\beta$  Ti. In relation to the stability of the  $\beta$  phase, the alloys can even possess the properties of shape memory and superelasticity. These qualities are courtesy of a reversible solid-state phase transformation called martensitic transformation which occurs by thermal (increase in temperature) or mechanical (relieving stress) means, from the martensitic phase; and leads to the shape memory effect and superelasticity respectively.<sup>22</sup> Some of the various Ti based superelastic alloys that have been developed and studied are Ti-Nb-Sn<sup>23</sup>, Ti-Nb-Al<sup>24</sup>, Ti-Nb-Ta<sup>25,26</sup>, Ti-Nb-Zr<sup>27,28</sup>, Ti-Nb-O<sup>29</sup>, Ti-Nb-Pt<sup>30</sup>, Ti-Mo-Ga<sup>31</sup>, Ti-Mo-Sn<sup>32</sup>, Ti-(8-10)Mo-4Nb-2V-3Al (mass%)<sup>33</sup>. Hence, this review article will explore the various new developments, for nickel free alternatives, in its limited capability.

### SHAPE MEMORY AND SUPERELASTICITY

#### **Metallurgic aspect:**

#### **Shape Memory Effect**

When the alloy is deformed at a temperature below the  $M_f$  (Martensite finish temperature) and subsequently heated to a temperature above the  $A_f$  (Austenite finish temperature), the shape is recovered. Martensite transformation by shape memory is thermally induced. On decrease of temperature from  $M_s$  to  $M_f$ , there is growth of existing martensite plates and nucleation of new ones. On increase of temperature from  $M_f$  to  $M_s$ , the inverse occurs, that is shrinkage and disappearance of plates. This confirms a stress-temperature equivalence, as both decrease in temperature and an increase in stress stabilize the martensitic phase.<sup>34</sup>

#### **Superelasticity- SIM**

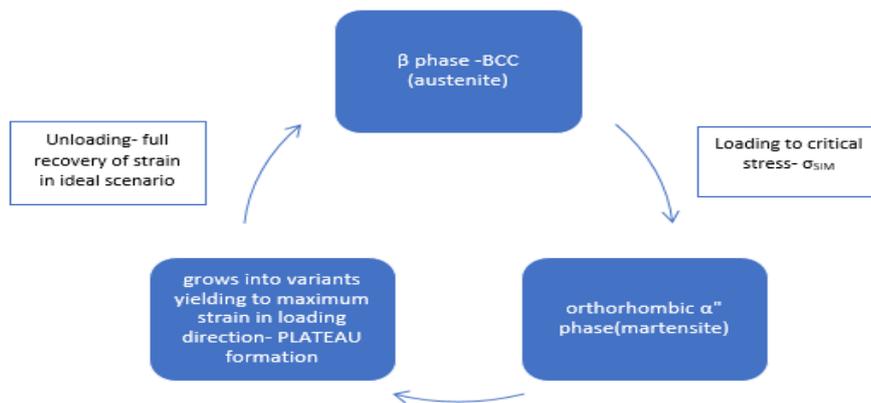


Fig. 1

**Schematic diagram representing SIM transformation in beta Ti**

Even at temperatures above  $M_s$ , Martensite can be formed on applying a certain amount of stress, and this is called SIM (Stress Induced Martensite) when the deformation occurs above  $A_s$  but below  $M_d$ . The stress required for SIM ( $\sigma_{SIM}$ ) is proportional to the Transformation temperature in various alloy systems [34, 24-26] obeying the Clausius-Clapeyron equation, that characterizes the discontinuous phase transition between two phases:

$$d\sigma/dT_\tau = \Delta H/T\varepsilon_0$$

$\Delta H$  – Transformation latent energy,  $T_\tau$  – Transformation Temperature,  $\sigma$  – stress,  $\varepsilon_0$  – Transformation strain parallel to direction of applied stress.

The stress required for SIM transformation is directly proportional to the temperature upto the critical desist temperature  $M_d$ , at which point, the stress required for martensitic transformation is greater than the critical stress required to activate motion of dislocations, meaning that the SIM transformation occurs between  $M_s$  and  $M_d$ .

The stress that is applied to the Austenite, gets retained and the material transforms to Martensite (loading) and the reverse occurs as the stress is released (unloading) and Austenite is formed. The crystallographic reversability, is on account of the martensite plate reversion due to backward shear. <sup>25</sup>

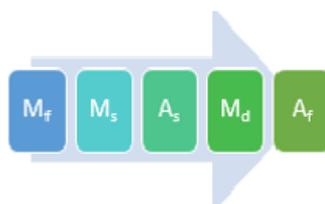


Fig. 2

**Schematic representation of the Temperature Transition Range**

**SUPERELASTICITY IN beta Ti ALLOYS**

In beta Ti, commercially available TMAs are not superelastic, and hence in this article the various alloying elements that are added, thermomechanical treatments and the crystallographic texture differences, and striking a balance between these factors, in order to influence and modify the physical and mechanical properties to offer a superelastic advantage are explored below.

**GENERAL COMPOSITION OF NEWER Ni FREE Ti BASED SUPERELASTIC ALLOYS**

CpTi (Commercially pure Titanium) can exist in two forms, alpha (stable hcp structure, below 822<sup>o</sup> C) and beta (stable bcc structure above 822<sup>o</sup> C). alpha stabilizers are those elements that’s stabilize the alpha-Ti microstructure. beta stabilizers like Vanadium (V), Molybdenum (Mo), Tantalum (Ta) are added to stabilize the beta-Ti microstructure at room temperature. beta Ti is preferred for orthodontic use, because of its lower elastic modulus and higher ductility than alpha Ti alloys, and is widely used in the form of TMA (Titanium Molybdenum Alloy). These newer alloys generally contain beta stabilizers, certain neutral alloying elements, and the structure is a metastable beta microstructure, where in, martensitic transformation occurs on application of stress (SIM transformation).

**ALLOYING ELEMENTS**

**beta stabilizers**

The beta phase stability and  $\sigma_s$  (critical stress for dislocation slip) are very critical for superelasticity and beta phase stability should fall within a very narrow range, low enough, to allow SIM transformation with twinning, high enough to retain a full beta phase on

rapid cooling to room temperature ( $M_s$  is below the room temperature)<sup>25</sup> and the critical stress for slip dislocation should be increased so that the martensitic transformation is preferred over slip dislocation. Only a small range of alloy compositions can offer this. Some examples are:

- Nb as  $\beta$  stabilizer: Ti-(22–25) at.% Nb alloys exhibiting shape memory effect and Ti-(25.5–27) at.% Nb alloys exhibiting superelastic behavior
- Mo as  $\beta$  stabilizer: (Ti-Zr)-Mo-Sn [35], Ti-Nb-Mo-Zr-Sn<sup>36</sup>
- Fe as  $\beta$  stabilizer: Ti-Zr-Nb-Fe<sup>37</sup>

Though Nb reduces the transformation temperature, it decreases the transformation strain, which has a negative impact on the superelasticity of the alloy.<sup>22</sup> This can be countered by addition of various ternary and quaternary elements, thereby reducing the Nb content. These elements basically decrease the martensite transformation temperature, ensure that there is a minimum decrease in the transformation stress and an increase in the critical stress for slip deformation, for improved superelastic properties. Addition of ternary alloying elements like Pt has also been studied and is said to be 4 times as effective as Nb, in reducing the  $M_s$  temperature and 3 times as effective than Nb, in reducing transformation strain<sup>30</sup>. The addition of Al, to the binary Ti-Nb has also been studied. Though it's an  $\alpha$  stabilizer, it enhances the shape memory and superelasticity of Ti-Nb alloys. With increase in Al content, the transformation temperatures decrease and superelastic behavior is observed at 24 at. % Nb, for Ti-xNb-3Al. Maximum recovery strain of over 4% observed in rolling direction, for Ti-24Nb-3Al. Various aspects of Ti-Nb-Al alloys have been studied<sup>24</sup>.

### Other Elements – Zr, Sn

$\beta$  Ti alloys with high recoverable strain (on thermomechanical treatment) have quaternary neutral alloying elements like Zr (though Zr isn't neutral in Ti-Nb based alloys) and Sn added so that: There is an increase in the recoverable strain ( $\epsilon_{rec}$ ) and a decrease in transformation temperatures. (less reduction in transformation strains and equal or more reduction in  $M_s$  on replacing  $\beta$  stabilizers like Nb and Ta. Ex. 1. There is an observable reduction in  $M_s$  of 35 K in Ti-22Nb<sup>38</sup> and 42 K in Ti-30Ta<sup>39</sup> per atomic % of added Zr. Addition of Zr, leads to the lowest reduction in transformation strain and similar reduction in  $M_s$ . Ex. 1. Ti-22Nb-6Zr with 6 at.% Zr, has increased  $\epsilon_{rec}$  from 3% in Ti-(26-27) at.% Nb<sup>41</sup> to 4.3% in Ti-22Nb-6Zr.<sup>28</sup> Ex. 2. Ti19.1Nb8.8Zr<sup>40</sup> exhibits reversible martensitic transformation and superelastic behavior, and has better corrosion resistance than NiTi and excellent biocompatibility (as reported in cell culture studies) and has a good potential for biomedical applications. Suppressing  $\omega$  phase and decreasing elastic modulus:  $\beta$  Ti superelastic alloys have a lower than average elastic modulus as opposed to the conventional Ti alloys, due to the plateau on the stress-strain curve which is caused by the SIM reversible transformation. The Intrinsic elastic modulus is related to the phases and their stability. Highest Elastic modulus is observed in the  $\omega$  phase, followed by the  $\alpha'$ ,  $\alpha''$  and  $\beta$  phase in that order.<sup>41-43</sup> The metastable athermal  $\beta$  phase is susceptible to conversion to  $\omega$  phase on quenching<sup>38</sup> and this would cause an increase in the elastic modulus of the material irrespective of whether the material is in an athermal/isothermal  $\omega$  phase. Isothermal  $\omega$  phase increases the recoverable strain<sup>44</sup> due to precipitation hardening that ultimately increases critical stress for dislocation slip but athermal  $\omega$  phase causes an increase in hysteresis, which negatively affects the superelastic properties<sup>38</sup>, so the actual effect of the  $\omega$  phase on the superelastic properties are not very clear. Ex. 3. Addition of Sn, reduces athermal  $\omega$  phase and reduces  $M_s$  temperature by 150 K per atomic % Sn in Ti-Nb-Sn alloys.<sup>39, 45, 46</sup>

### Interstitial Alloying Elements

One of the major drawbacks of just the binary Ti-Nb system were the low critical stress for slip. Substitutional alloying elements like Zr, Ta, Al, Pt and Sn do not have much effect on the critical stress for slip.<sup>19</sup> Interstitial elements like O, N and B increase the critical stress for slip and also improve the superelasticity. They are used for maintaining the  $\beta$  phase stability, lead to a suppression of  $\alpha''$  phase and a decrease in the  $M_s$  temperature<sup>47-50</sup> Ex. 1% O addition to Ti-22Nb and Ti-Nb-Ta-Zr alloy systems decreases  $M_s$  by 160K<sup>51</sup> addition of N, has a similar effect with respect to the  $M_s$  and suppression of the  $\alpha''$  phase. Also observed is an increase in the critical stress for slip dislocation, improving the super-elasticity.<sup>49</sup>

### Heat treatment

Superelastic properties of the Ti-Nb alloy can be improved by thermo-mechanical heat treatment, when it is heated to a temperature below the recrystallization temperature, following severe cold-working. Aging can also be carried out, by heating between 473 and 673 K which increases the critical stress for slip dislocation (fine and dense  $\omega$  precipitates) and stabilizes the superelasticity.  $\omega$  phase isn't very beneficial for the mechanical properties of Ti based alloys, but  $\omega$  precipitates (10-50 nm) improve the superelasticity without affecting the ductility.<sup>44</sup> Low temperature annealing followed by aging, leads to excellent superelastic properties due to the combination of work hardening and age hardening.

### Crystallographic texture

$\beta$  Ti alloys have excellent cold-workability and the texture evolution during cold working and the heat treatment influence the superelasticity. The Superelastic properties are highly influenced by the crystallographic orientation density due to the varying amounts of strain in the different axes. (Bulk of the transformation strain distributed among the various crystallographic orientations) This anisotropy with textural evolution shows improved superelastic properties and is observed in, but is not unique to Ni free Ti based superelastic systems.<sup>53, 54</sup> It's also observed in Cu<sup>55</sup> and Fe<sup>56</sup> based superelastic alloys, and NiTi<sup>57</sup>.

**Orthodontic applications of shape memory archwires****Ti-Nb-Al**

Two animal studies have been conducted to evaluate the application of Ti-Nb-Al (Ti-24Nb-3Al) in rats to compare the efficacy of this superelastic alloy with NiTi. The studies compared palatal<sup>58</sup> and buccal<sup>59</sup> tooth movement with springs, of both NiTi and Ti-Nb-Al. Both of them concluded that the efficiency in tooth movement of the Ti-Nb-Al alloy was comparable with that of NiTi, with the added advantage of being biocompatible, and hence would make an excellent alternative to NiTi as a Ni free Shape Memory Alloy.<sup>58,59</sup> In one of the studies, it was found that the initial force magnitude of the Ti-Nb-Al springs was almost half that of NiTi, hence the forces exerted would be lighter, and continuous, rather than the step-wise fashion observed in NiTi. After 17 days, there was practically no difference in the tooth movement when compared with NiTi.<sup>59</sup> Hence these could be tested further in-vivo, for longer periods and more varied applications so that they could prove to be an effective substitute to NiTi.

**SMPUs**

Jung in 2008 studied the application of Shape Memory Polyurethane in Orthodontics. The archwire was formed by melt-spinning a block of Polyurethane copolymer and this was synthesized from 4,4'-methylene bis(phenylisocyanate), poly( $\epsilon$ -caprolactone) diol (PCL), and 1,4-butanediol. It had observable high shape recovery force (70 gf at 40% hard segment content) which was preserved even after one month following the shape recovery test, at a constant temperature of 50<sup>0</sup> C. In the first 2 hours there was an exponential decrease in the shape recovery force, but it reached an equilibrium and stabilized at 50 gf at around 20 days of treatment. Orthodontic tests were carried out on the model (*in-vitro study*) and alignment of mal-aligned teeth was possible.<sup>60</sup> Further studies conducted by Liu et al in 2017 and 2018 showed that there was an inevitable decrease in force applied when compared to a metal wire, though the recovery force was within the required magnitude in plain SPMUs<sup>61</sup> and hence strengthening by reinforcing with filler materials like Glass Fiber, forming Glass Fiber Reinforced Shape Memory Poly-Urethane (GFRSMPU) was done. GFRSMPU, showed a significant improvement in the mechanical properties along with preservation of shape memory.<sup>62</sup> These polymer archwires could be part of novel orthodontic treatment practices, and provide an aesthetically satisfactory appearance, along with increased biocompatibility and the advantage of shape recovery in oral temperatures, during the course of orthodontic treatment.

**CONCLUSION**

Ti based superelastic alloys, have various biomedical and non-medical applications, due to their superior mechanical properties, like low elastic modulus, increased corrosion resistance and hence improved biocompatibility. They have a vast unexplored potential in relation to dental applications, as only in-vitro and animal studies have been conducted until now, and they have to undergo clinical trials before being commercialized. Some of the most popular bio-medical applications apart from dental use are load bearing implants and self-expanding stents. With further research and clinical trials with Ni free superelastic alloys, the entire profile of shape memory alloys could change. Apart from shape memory alloys, newer non-metallic Poly-Urethane based polymeric archwires have also been extensively studied(*in-vitro*), and have very recently been reinforced with Glass fiber, for improved mechanical properties.

**CONFLICT OF INTEREST**

Conflict of interest declared none.

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