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A Review on Titanium-Niobium Shape Memory Alloys (SMA)

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Abstract—*Shape memory alloys (SMA) are fascinating materials, which exhibit the shape-memory effect and superelasticity not common for ordinary metals. The former effect is the ability to recover automatically a certain shape, whenever the external conditions are identical to those under which the material has been trained. The broad range of applications includes sensors and actuators in medicine and astronautics. At present the research on the increasing interest to the titanium-niobium alloys is caused by combination of their unique properties: thermal stability, superconductivity, corrosion firmness, shape memory, etc. Titanium-niobium (TiNb) SMAs have recently been proposed as an alternative to NiTi SMAs due to the biocompatibility of both constituents, the ability of both Ti and Nb to form protective surface oxides, and their superior workability. This paper gives the review of basic concepts of shape memory alloys, mode of metal transformation. Further the extensive application of TiNb SMA is discussed in the study. The Mechanical properties of the material also focused.*

Keywords*: SMA, TiNb, SME, Microstructure, Mechanical properties.*

1. INTRODUCTION

Shape Memory Alloys (SMA's) are novel materials which have the ability to return to a predetermined shape when heated. When an SMA is cold, or below its transformation temperature, it has a very low yield strength and can be deformed quite easily into any new shape, which it will retain. However, when the material is heated above its transformation temperature it undergoes a change in crystal structure which causes it to return to its original shape. If the SMA encounters any resistance during this transformation, it can generate extremely large forces.

The first reported steps towards the discovery of the shape-memory effect were taken in the 1930s. According to Otsuka and Wayman, A. Ölander discovered the pseudoelastic behavior of the Au-Cd alloy in 1932. Greninger and Mooradian (1938) observed the formation and disappearance of a martensitic phase by decreasing and increasing the temperature of a Cu-Zn alloy. The basic phenomenon of the memory effect governed by the thermoelastic behavior of the martensite phase was widely reported a decade later by Kurdjumov and Khandros (1949) and also by Chang and Read (1951). [1]

The nickel-titanium alloys were first developed in 1962–1963 by the United States Naval Ordnance Laboratory and commercialized under the trade name Nitinol (an acronym for Nickel Titanium Naval Ordnance Laboratories). Their remarkable properties were discovered by accident. A sample that was bent out of shape many times was presented at a laboratory management meeting. One of the associate technical directors, David S. Muzzey, decided to see what would happen if the sample was subjected to heat and held pipe lighter underneath it. To everyone's amazement the sample stretched back to its original shape. [2][3]

There is another type of SMA, called a ferromagnetic shape-memory alloy (FSMA), that changes shape under strong magnetic fields. These materials are of particular interest as the magnetic response tends to be faster and more efficient than temperature-induced responses.

2. SHAPE MEMORY EFFECT AND SUPER ELASTICITY IN TITANIUM – NIOBIUM (TI-NB) BASED ALLOYS

The study of TiNb-based alloys that are suitable materials for substitution of TiNi in many biocompatible applications. Niobium is β stabilizer, so that the TiNb falls into β -Ti alloys, eventually into β rich (α+β) alloys. Nevertheless, it has been confirmed for wide range of Nb content (16.7 - 50 wt.% Nb) that TiNb alloys exhibited at room temperature the shape memory effect and superelastic behavior that is related to stress induced martensite. [4-6]

TiNb binary alloys exhibit SME and SE at room temperature, and their superelastic properties considerably improved by thermo mechanical treatment. The superelastic properties of TiNb alloys can be improved by the addition of alloying elements such as Zr, Ta, Pt, O, etc. It is well known that the mechanical properties of Ti-Nb alloy can be futher improved by addition of alloying elements to this binary alloy. During last ten years Ti-Nb-X (X= Sn, Zr, Ta, Mo, Pt, Pd, Au, Al, Ga, Ge, O, Hf) alloy has been developed and shape memory effect and superelasticity were investigated systematically by the researchers.

3. RECENT INVESTIGATIONS

Table 1 shows the recent investigations and developments in Ti-Nb based shape memory alloys.

Table 1: Existing investigations on Ti-Nb based SMA

S.No.	Author (Year)	Ti-Nb based alloy	Investigation
1	Shuichi Miyazaki (2004)	Ti-Nb	Mechanical Properties and Shape Memory behavior of Ti-Nb Alloys
2	Yusuke Fukui (2004)	Ti-Nb-Al	Mechanical Properties of a Ti-Nb-Al Shape Memory Alloy
3	Shuichi Miyazaki (2005)	Ti-Nb-O	Shape Memory behavior of Ti–22Nb–(0.5–2.0) O(at%) Biomedical Alloys
4	D.H.Ping (2006)	Ti–30Nb–3Pd	TEM investigations on martensite in a Ti–Nb-based shape memory alloys
5	Cui'e Wen (2009)	Ti-Nb	Nanohydroxy apatite coating on a titanium–niobium alloy by a hydrothermal process
6	S. Miyazaki (2010)	Ti–Nb–Mo	Shape memory properties of Ti–Nb–Mo biomedical alloys
7	I.Karaman (2010)	Ti74-Nb26	Superelastic memory effect of Ti-Nb
8	L.W. Ma, C.Y. Chung, Y.X. Tong, and Y.F. Zheng (2011)	Ti-Nb-Zr	Properties of Porous TiNbZr Shape Memory Alloy Fabricated by Mechanical Alloying and Hot Isostatic Pressing
9	Mariah S. Hahn (2012)	Ti-Nb	Comparative study on corrosion resistance of TiNi and TiNb
10	V. Brailovski (2013)	Ti-Nb-Zr and Ti-Nb-Ta	In situ X-ray diffraction strain-controlled study of Ti–Nb–Zr and Ti–Nb–Ta shape memory alloys
11	L. KUNČICKA, P. ŠTĚPAN, J. KLIBER, I. MAMUZIČ (2013)	Ti-Nb	Influence of heat treatment on properties of Ti-Nb alloys
12	L.W. Ma (2013)	Ti-Nb-Zr and Ti-Nb-Zr-Mo	Superelastic behavior and microstructure of Ti19Nb9Zr1Mo (at%) alloy
13	H. Shi (2014)	Ni-Ti-Nb	Site occupation of Nb atoms in ternary Ni-Ti-Nb SMA

Shape memory alloys have been a major boom to industry advanced since its inception. In spite of its history, it has found widespread applications in diverse industries. The improvements on Ti-Nb based SMA's listed in Table 1 have the following conclusions:

1. Shuichi Miyazaki (2004) concluded that the martensitic transformation start temperature decreased by 43K with 1 at % increase of Nb content. The shape memory effect and superelastic behavior were observed in Ti-(22–25) at % Nb alloys and Ti-(25.5–27) at % Nb alloys, respectively, subjected to solution treatment at 1173K for 3.6 ks, respectively. Neither shape memory effect nor superelastic behavior was observed in Ti-(28–29) at % Nb alloys.

The critical stress for inducing martensitic transformation increased with increasing test temperature. The enthalpy and entropy for the martensitic transformation were estimated to be 340 J/mol and 1:30 J/mol-K, respectively.

The maximum recovered strain of 3% was obtained at room temperature in the solution treated Ti-(25–27) at % Nb alloys. The low critical stress for slip deformation caused the superelasticity not to reveal a large strain. The aging treatment at 573K for 3.6 ks increased the critical stress for slip and stabilized the superelastic behavior of Ti-Nb alloys.

2. Yusuke Fukui (2004) concluded that although the dislocation was not observed but fine particles are observed in TiNbAl. These particles must be a thermal which is commonly exists in Ti-Nb binary alloys.

TiNbAl alloy exhibits superelasticity regardless of the tensile direction. Superelastic strain of 4.7% was observed when the tensile direction was parallel to RD, and only 1.3% of superelastic strain was observed when the tensile direction was parallel to TD. A large superelastic strain of 4.7% was successfully brought out.

The stress for inducing martensite(SIMT) becomes lower and superelastic(SE) strain becomes larger with increasing the number of deformation cycles. This is due to the training effect.

σ_{SIMT} becomes larger and ε_{SE} becomes smaller with increasing the angle between the tensile direction and RD, comparing at the same number of deformation cycles.

3. Shuichi Miyazaki (2005) concluded that in order to develop Ni-free Ti-based biomedical shape memory alloys, the Ti–22 at %Nb–(0.5–2.0) at %O alloys were investigated to clarify the effect of addition of oxygen to the Ti–Nb binary alloy on shape memory behaviour and mechanical properties. The obtained results are as follows:

Adding oxygen to the Ti–Nb binary alloy causes increasing fracture stress and decreasing fracture strain because of solid-solution hardening effect. The maximum fracture stress of 1.37 Gpa is obtained in the case of an as-rolled Ti–22 at %Nb–2.0 at %O alloy.

The transformation temperature in the Ti–22 at %Nb–(0–2.0) at %O alloys increases by 200K with 1 at % increase of oxygen. Comparing to the Ti–O binary system, the effect of adding oxygen for increasing the transformation temperature is more effective in the ternary Ti–Nb–O system.

The martentsitic transformation start temperature decreases by 160K with 1 at % increase of oxygen content. The shape memory effect and superelasitc behaviour are observed in the Ti–22 at %Nb–(0–0.5) at %O alloys and the Ti–22 at %Nb–(1.0–1.5) at %O alloys, respectively.

The critical stress is increases up to 890 Mpa in a Ti–22 at %Nb–1.5 at %O alloy with increasing oxygen content. The maximum total recovery strain decreases from 4% in a Ti–22 at %Nb–0.5 at %O alloy to 3% in a Ti–22 at %Nb–1.5 at %O alloy with increasing oxygen content. It is confirmed that adding oxygen to the Ti–Nb binary alloys causes increasing in the critical stress for slip due to solution hardening effect. [7-9]

4. D.H.Ping (2006) concluded that plate-shaped martensitic ω phase in Ti-based alloys can be formed during water-quenching. The formation of the plate-shaped ω phase is suggested to be related with the stability of the metastable β phase due to the Pd addition, which suppresses the coarsening of particle-like ω phase. The retained β phase, and plate-shaped and also particle like martensitic ω phase are fully transformed to α'' martensite with a $(110)_{\alpha''}$ twin structure during deformation at room temperature. It is suggested that the ω transforms into α'' through β.

5. Cui'e Wen (2009) concluded that the study demonstrates a layer of nano-HA can be effectively and efficiently coated onto the surface of an Ni-free Ti SMA through a hydrothermal process. The Ca/P solution used in the hydrothermal process is proposed and used for the surface coating for the first time. The ionic composition of this innovative solution is significantly simpler than that of SBF solutions. The hydrothermal process requires a low temperature and eliminates the chemical pre-treatment used in traditional bio mimetic processes. The HA particles in the coating layer exhibits a polygonal shape with sizes less than 100 nm. A hydrothermal treatment at a temperature of 200 ^{0}C held for 12 h results in a nano - HA coating with excellent crystallinity.

6. S. Miyazaki (2010) concluded taht the reverse martensitic transformation finish temperature Af of the Ti–(21, 22)Nb alloys decreases by an average of 90 K with the addition of 1 at.% Mo. However, the Af of Ti–21Nb, Ti–17Nb–1Mo and Ti–14Nb–2Mo decreases by 30, 30 and 25 K, respectively, per at.% increase in Nb content.

Larger calculated transformation strain is attainable in a ternary alloy with Af similar to that of the binary one.

The Ti–27Nb, Ti–24Nb–1Mo, Ti–21Nb–2Mo and Ti–18Nb–3Mo alloys exhibit the most stable SE with a narrow stress hysteresis among Ti–Nb–Mo alloys with Mo contents of 0, 1, 2 and 3 at.%, respectively. The critical stress for slip deformation is increases linearly on increasing Mo content, owing to the increase in the volume fraction of the omega phase as well as the solid solution hardening effect of Mo.

The maximum recovery and transformation strains increase on increasing Mo content. The effect is related to the increases in both the critical stress for slip deformation and the transformation strain.

7. I.Karaman (2010) concluded that the superelastic memory behavior first observed in nickel-rich Ni–Ti SMAs is also observed in the Ti74Nb26–SMA.

8. L.W. Ma, C.Y. Chung, Y.X. Tong, and Y.F. Zheng (2011) concluded that Ti-22Nb-6Zr (at.%) shape memory alloy was successfully fabricated using both MA together with HIP methods. Nearly spherical pores distributed on the cross section of the HIP TiNbZr alloy were obtained. Martensitic phases were found in the HIP-TiNbZr alloy and further confirmed by its lamellar morphologies. Moreover, nearly complete superelasticity and 3% recoverable elastic compressive strain was achieved after mechanical cycling.

9. Mariah S. Hahn (2012) concluded that Ti–26Nb SMAs may be promising alternatives to Ni–49.2Ti SMAs for certain biomedical applications.

10. V. Brailovski (2013) concluded that during the cooling and heating of TNT and TNZ alloys, reversible anisotropic α″-phase X-ray line shifts are observed. On heating, α″-phase LPs strive towards corresponding parent β-phase LPs. These variations can be observed regardless of the absence or the presence of external stresses, being less pronounced for TNZ than for TNT alloys.

In the −150 °C–RT heating range, crystallographic resource of recovery strain decreases from 5.7 to 4.5% (TNZ) and from 3.5 to 2.5% (TNT) following the single-crystal calculation approach.

Under strain-free cooling, an additional quantity of α″-phase forms in TNT, while both "athermal" α″- and ω-phases form in TNZ. Cooling under stress of both alloys is accompanied by an increase in the quantity and reorientation of α″-phase. Application of an external load at −150 °C results in a certain growth of α″-phase content, while the quantity of ω-phase (TNZ) does not seem to be affected.

Strain-free heating of TNT alloy results in reverse α″→β transformation, whereas during heating under stress, α″ →β transformation is preceded by α″-phase reorientation. Strain-free heating of TNZ alloy results in simultaneous α″ →β and ω→β transformations, whereas heating under stress results in sequential two-step transformation:ω→β + β→α″ (or β + ω→α″), followed by α″→β.

The appearance and disappearance of inhomogeneous microstresses, either under load at constant temperature or during strain-free or constant-strain cooling–heating cycles are exclusively related to the formation and disappearance of thermoelastic α″-martensite in the parent β-phase.

11. L. KUNČICKA, P. ŠTĚPAN, J. KLIBER, I. MAMUZIČ (2013) concluded that, four groups of samples of a titanium alloy with alloying niobium content of 20,7 (at)% were annealed on air at the temperature of 800 °C for 15, 30, 45 and 60 minutes and after alloying they were subjected to oxygen content observation, microhardness measurements and OM. The results proved that annealing time is of an indispensable influence on the oxygen content – it increased from 0,207 % in the initial condition after forming (sample group A) up to 1,127 % after annealing for 60 minutes (sample group E). Together with increasing oxygen content microhardness increased from 218 HV at the A sample to 306 HV at the E sample group.

12. L.W. Ma (2013) concluded that new strain glass alloy, Ti19Nb9Zr1Mo(at%), shows agreat difference in microstructure and exhibits a combi- nation of a good superelasticity of ~3.1% and complete SME at room temperature. The mechanism of this superelasticity is related to the randomly distributed point defect which opposes to the formation and growth of the favorable single variants.

13. H. Shi (2014) concluded that Nb occupancy in austenite B2-NiTi matrix and Ti2Ni phases was investigated via HAADFHRSTEM and PED. Nb prefers to occupy the Ti site rather than the Ni site. Theoretical investigations within DFT confirm that the Nb formation energy on the Ti site is lower than that on the Ni site.

4. TESTS

(a).Mechanical Properties

The prepared dog-bone specimens were exposed to uniaxial tension for the TiNb samples. Strain was measured with an extensometer attached directly to the specimen, and the austenite modulus of each SMA was taken as the slope of the stress–strain curve.

(b). Corrosion resistance

Potentio-dynamic tests were performed on SMA samples to know how they are corrosive.

(c). Microhardness measurement

Microhardness measurements were performed on samples to observe the influence of certain heat treatment processes.

(d). Optical metallography

Optical metallography was focused on observation of microstructure and the phases.

(e). SEM-EDX analysis

The SEM-EDX analysis provides the information about the final content of chemical composition in the alloy (at)%.

(f).X-Ray Diffraction

Phase constitutions for shape memory alloys were investigated by XRD after solution treatment.

Concluding remarks

The goal of the present work was to investigate the following features of Ti–Nb based SMAs: (1) cytocompatibility, (2) corrosion resistance, and (3) alterations in surface composition following prolonged exposure to physiological solutions.The transformation strains of the NiTi alloys are at least twice as large as that of TiNb. This means that TiNb SMAs are not suitable for applications requiring transformation strains greater than approximately 3.3%. However, this constraint still means that TiNb samples can be used in bone applications, given that bone itself exhibits 2% recoverable strain. The superelastic memory behavior first observed in nickel-rich Ni–Ti SMAs is also observed in the Ti74Nb26–SMA. The Ti–27Nb, Ti–24Nb–1Mo, Ti–21Nb–2Mo and Ti–18Nb–3Mo alloys exhibit the most stable SE with a narrow stress hysteresis. TiNb based shape memory alloys are used for many biomedical applications. Several important key problems and issues remain to be addressed are given as below:

1. Roughness studies of Ti-Nb based Shape memory alloys.
2. Future work will be to find the effect of graphene layers of Ti-Nb based SMA.
3. Microstructure and mechanical properties of Ti-Nb based alloys.
4. Perform X- ray diffraction study of all Ti-Nb based alloys.
5. Surface integrity evolution from main cut to finish train cut in wire-EDM of TiNb based shape memory alloys.
6. Creep analysis on Ti-Nb based SMA.
7. Comparative studies on different manufacturing methods for Ti-Nb based SMA.
8. The corrosion resistance of heat treated Ti-Nb based alloys.
9. Bonding strength of Ti-Nb SMA (Lap joint.etc.).

10. Laser welding of TiNb SMA dissimilar and similar.
11. Surface characterization and wear behaviour of Ti-Nb SMA.
12. Analysis on Laser machined SMA.

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