Dynamics of martensitic structure at TiNb-based quenched alloys under heating and loading

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Abstract. Phase competition at TiNb-based Ni-free shape memory alloys caused by changes of alloying, temperature, external stresses is considered by analysis of experimental results on elastic modulus determination, X-ray diffraction, thermal analysis, mechanical tensile and indentation testing. Martensitic $\beta \leftrightarrow \alpha''$ transformation undergoes due to a reversible displacements of atoms at (002) plane of orthorhombic unit cell. The martensitic structure has high stability against thermal and mechanical cycling.

1. Introduction
It is well known that there are only two stable phases in pure Ti and solid solutions on its base: high temperature cubic (bcc) $\beta$-phase and low temperature hexagonal $\alpha$-phase. However, some other metastable phases could be formed dependent on alloying, heat treatment and pressure processing, as well as due to contamination by impurities [1].

Ternary and quaternary Ti–Nb-Zr, Ti–Nb-Ta, Ti–Nb-Ta-Zr alloys have been extensively investigated during the last years and the results confirm the possibility to obtain Ni-free, Ti-based solid solution alloys with shape memory effects (SME) connected with reversible $\beta \leftrightarrow \alpha''$ martensitic transformation [2,3].

The tailoring of metastable structures via reasonable processing yields inelastic phenomena as shape memory, pseudo-elasticity, high damping capacity, negative temperature dependence of electric resistivity etc. The shape memory alloys are attractive for medical applications as metallic implant materials combining superelasticity with biocompatibility comparable to that of pure Ti [4]. It is due to the both reasons: all the metals and their oxides are friendly for human body and the quenched alloys manifested excellent functional properties, including low elastic moduli closed to that of the human trabecular bone.

Other interesting feature of the Ti-Nb based alloys is a high thermal stability of the orthorhombic $\alpha''$ martensite. This is good for some technical applications based on high temperature SME as well as to study model alloys having reversible martensitic transformation in wide temperature range.

In this work phase transitions and products of martensitic transformation of biocompatible quenched Ti-Nb-Ta(Zr) alloys, especially metastable orthorhombic $\alpha''$ and cubic $\beta$ phases have been studied by elastic E and G moduli determination, thermal analysis (DTA), X-ray diffraction, tensile tests and nanoindentation to monitor the their structure dynamics and reversibility.
2. Factors of martensitic transformation

2.1. Alloying of solid solution by substitution elements

Pure titanium (α-Ti) has hexagonal lattice cell (P6_3/mmc) and undergoes at 882 °C at heating a phase transformation to body centered cubic, or β Ti (bcc, Im3m). Alloying of Ti by bcc isomorphous elements (Nb, Ta, Mo etc.) retards the diffusion and decreases the temperature of transformation as one can observe at Fig. 1a, monitoring the temperature range of endothermal peak.

Fast cooling of the high temperature bcc β-Ti yields metastable α”-martensitic phase due to a shear-like formation of the orthorhombic unit cell (Fig.1b) according to Bagariatskii schematic [5]. It implies that martensitic β→α” transformation undergoes due to a reversible subnano scale displacements of atoms at (002) plane of orthorhombic unit cell. So, alloying of Ti by bcc elements (Nb, Ta, Mo etc.) changes structure type of quenched solid solution on the way of rearrangement from hexagonal (alfa) phase till (cubic) beta phase.

![Figure 1](image)

Figure 1. The effect of alloying on endothermal effect and temperature range of martensitic transformation studied by differential thermal analysis, DTA (a) and distortion of orthorhombic lattice cell (b) on data of X-ray diffraction. Thermal curves marked a, b, c, e, f correspond to four typical alloys shown at right plot and at Table 1.

As shown at Fig.1b and at Table 1 and Table 2 α”-martensite is found at wide range of concentrations intermediated between stable α-Ti and β-Ti phases. Each composition can be characterized by unique set of parameters of lattice cell as well as a degree of its rhombic distortion R.
Table 1: Experimental parameters of unit cell (x10 nm) in quenched Ti-Nb-Ta alloys

| Phase | Symbol | a' | a'' | β | β' |
|-------|--------|----|-----|---|----|
| Space Group | p63/mmc | Cmcm | Im3m | Im3m |---|---|
| Conventional Presentation | a | 2.93 | 3.051-3.198 | 3.285 | 3.303 |
| | b | --- | 4.949-4.785 | --- | --- |
| | c | 4.77 | 4.673-4.650 | --- | --- |
| Orthorhombic Presentation | a | 2.93 | 3.051-3.198 | 3.285 | 3.303 |
| | b | 5.07 | 4.949-4.785 | 4.645 | 4.657 |
| | c | 4.77 | 4.673-4.650 | 4.645 | 4.657 |
| Degree of Rhombic Distortion | R=\sqrt{3a'/b} | 1 | 1-1.16 | 1.225 | 1.225 |

Table 2: Chemical composition of the quenched Ti-Nb-Ta alloys

| Alloy composition | Symbol | Rhombic distortion, R |
|-------------------|--------|-----------------------|
| Ti_{82.5}Nb_{4.4}Ta_{13.1} | a | 1.08 |
| Ti_{82.5}Nb_{7.5}Ta_{7.5} | b | 1.08 |
| Ti_{82.5}Nb_{17.5} | c | 1.10 |
| Ti_{75}Nb_{18.9}Ta_{2.1} | d | 1.12 |
| Ti_{75}Nb_{8.75}Ta_{6.25} | e | 1.15 |
| Ti_{75}Nb_{25} | f | 1.225 |

2.2. Dynamics of martensitic structure at heating
Distortion $R$ of orthorhombic $\alpha''$-martensite is also sensitive to temperature changes with the same way as to alloying. As one can see at Fig. 2 $R$ increases with increasing of temperature and degreases at cooling back. Heating is also causes the softening of elastic E and G modulus, they go down to the minimal values (E<60 GPa) within the $A_t-A_f$ range of reversible martensitic transformation $\beta \leftrightarrow \alpha''$. However, above $A_f$ temperature $\beta$-phase became the stable one and elastic modulus increases.

It was found [6] two composition ranges of the formation orthorhombic martensite which is stable to heating to secure the reversible martensitic transformation at heating, namely at range 80-240 °C and 450-550 °C. Between the ranges (250-450 °C) a concurrent metastable $\omega$-phase forms at heating. Formation of hexagonal $\omega$-phase above 300 °C could be monitored at Fig. 1a (curves c and d) and at Fig. 2 as pronounced exothermal effect on $\Delta Q$-curve which is correlated with sharp increase of $E$-modulus.

2.3. Mechanical behaviour of quenched alloys at loading
The mechanical behavior of the alloys depends on the chemical, phase and structure composition. Quenched alloys with $\beta$-phase structure (like $f$-alloy) manifest superelastic behavior due to stress-induced $\beta \leftrightarrow \alpha''$ transformation started at low (ca. 100 MPa) external stresses as shown at Figure 3. The alloys with $\alpha''+\beta$ martensitic structure (like $e$, $d$ alloys), are able to accumulate deformation via rearrangements of martensite structure, and then undergo shear transition induced by external stresses. They recover the accumulated deformation by shape memory effect at subsequent heating.

Crystallographic reserve of recoverable deformation at the $\beta \leftrightarrow \alpha''$ transformation in the alloys was estimated up to 3.5% returnable deformation [7]. The results were analyzed taking into account XRD data on phase composition and degree of distortion $R=\sqrt{3a'/b}$ of orthorhombic $\alpha''$-martensite (Cmcm space group) according to Yu.A. Bagariatskii’s model of $\beta \rightarrow \alpha'' \rightarrow \alpha'$ transition [5].

It was found that experimental realization of superelasticity (up to 2.5 % of returnable deformation) was close to its theoretical limit [7] and it was observed at alloys having extremely low Young’s modulus (about 60 GPa and less) and the largest rhombic distortion (about $R=1.16$) of unit cell.
Figure 2. Thermal effects and changes of Young modulus at heating of quenched Ti-Nd-Ta alloys (left) and progressive rhombic distortion of unit cell (right) at heating through $A_s-A_f$ range.

Figure 3. Examples of superelastic behaviour of tempered Ti$_{74.5}$Nb$_{19.7}$Ta$_{5.8}$, the starting pseudo yield stress is shown for each curve.

Figure 4. The effect of distortion of orthorhombic unit cell at quenched Ti-Nb-Ta alloys on starting pseudo yield stress.
3. Conclusions

Reversible martensitic $\beta \leftrightarrow \alpha''$ transition is observed at the Ti-Nb-Ta quenched alloys at thermal and loading cycling. There are two sequential mechanisms of reversible accumulation of deformation: lattice distortion of orthorhombic martensite and $\beta \leftrightarrow \alpha''$ phase transition. Reversible phase transition is exhibited by the definite alloys characterized by high distortion of unit cell, extremely low elastic moduli and excluding a formation of concurrent metastable $\omega$-phase.

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