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Study of some heat treatment effects on thermodynamic and structural properties of Ti-Ta biomedical shape memory alloys

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Abstract. The shape memory effect (SME) in binary β -Ti alloys is associated with a reversible martensitic transformation from α'' - orthorhombic martensitic phase to β -bcc austenitic phase. The present paper reports the experimental results obtained on TiTa alloys, containing 25, 30, 35 and 50 mass % Ta. The specimens were processed from as-cast levitation induction melt ingots, cut by wire electric discharge, hot/ cold rolled (enabling to obtain 500-mm long thin ribbons), solution treated (900°C/ 30 min/ water quenched, W.Q.) and aged (300°C/ 1 h/ W.Q.). From each heat treated state, samples were cut for tests meant to emphasize the presence of thermal and mechanical memory behaviour. Thermal memory was highlighted by SME-work generating training cycles, investigated by cinematographic analysis. The respective results were corroborated with those recorded by dynamic mechanical analysis (DMA). Mechanical memory was revealed by winding-unwinding and tensile tests. The winding and tensile tests offered information about the capacity of cold rolled ribbons to memorize their room temperature (RT) profile. Tensile tests were applied up to complete failure or by RT loading-unloading cycles.

1. Introduction

Ti-Ni shape memory alloys (SMAs), discovered in 1962, experience shape memory effect (SME) superelasticity and biocompatibility which enabled their use for health-care and biomedical devices, but the risk of Ni allergy and hypersensitivity for long-term use urged the development of Ni free Ti based SMAs [1].

In order to decrease the elastic moduli of Ti based SMAs (55–85 GPa) such as to render it as close as possible to that of a human bone (10–28 GPa) [2] and to avoid the formation of ω phase [3] Ta alloying was investigated.

At Ti-Ta SMAs, shape recovery phenomena are based on the reversible $\beta(B2) \leftrightarrow \alpha''(B19)$ orthorhombic) martensitic transformation, occurring between room temperature (RT) and 230°C, with a decreasing tendency, of critical transformation temperatures, of 30°C per each raise of 1 at.% Ta [4]. The investigation of chemical composition effects, between 10 and 40 mass % Ta, has shown that for amounts between 22 and 26 mass% % Ta, α' -hexagonal close packed (hcp) martensite is formed [5].

The best results, from the point of view of SME, have been obtained in the composition range Ti-(30-40) at. % Ta and the alloys containing less than 35 at. % Ta, that have the critical temperature for the start of direct martensitic transformation (M_s) above 373 K, are considered as high-temperature SMAs [6]. Nevertheless, the application of ageing heat treatment to Ti-30 at. % Ta, the alloy with the



highest transformation temperature, a 100-degree decrease of M_s -temperature was reported [7].

Since the Ta concentration limit between the chemical compositions that enhance the formation of α' -hcp and α'' -B19 martensites was not very clear, systematic studies were performed concerning Tantalum amount effects on structural and mechanical properties. Thus, α'' -B19 martensite was observed at Ti-50 mass % (equivalent to about 20.9 at %) Ta [8] as well as at Ti-25 mass % Ta, which was reported to experience mechanical compatibility for biomedical applications [9].

Considering that the thermal stability of binary Ti-Ta alloys is insufficient [10], that most of the studies were focussed on Ti-30 at % (~ 61.8 mass %) Ta SMAs [11] for which no systematic studies concerning work generating SME [12] were reported, the present study aims to discuss heat treatment effects on the thermal and mechanical memory behaviour of Ti-Ta containing less than 50 mass % Ta and to emphasize their capacity to develop work during thermal cycling.

2. Experimental procedure

Ingots with four chemical compositions were remelted five times in a cold crucible induction furnace and cast into copper moulds. After each remelting, composition corrections were performed such as to achieve the nominal compositions Ti-(25, 30, 35 and 50) mass % Ta, respectively. The ingots were cut by wire spark erosion, hot rolled to 1.2 mm-thickness at 600°C and cold rolled to thicknesses between 0.8 and 0.2 mm (ribbons exceeding 500 mm in length being obtained). Figure 1 illustrates the chemical compositions of the four experimental alloys, which were designated as 25Ta, 30Ta, 35Ta and 50Ta, respectively and the correspondence between mass and atomic % [13].

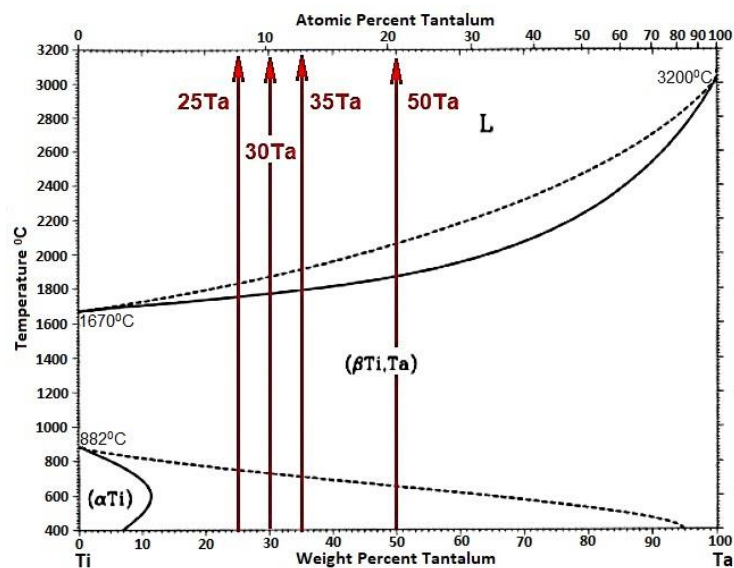


Figure 1. Illustration of the chemical compositions of the Ti-Ta experimental alloys.

By wire spark erosion, two tensile specimens with gauge dimension 4×20 mm and four rectangular specimens 4×20 mm and 4×50 mm, respectively were cut, from each of the four chemical compositions before being solution treated (900°C/30 min/ water quenched, WQ). One specimen of each type and composition was aged (300°C/1 h/ WQ).

The rectangular specimens with dimensions 4×50 mm, weighing 1 g, were trained, with a 125 g load fastened at their free end, by heating-cooling cycles. At RT, the specimens were martensitic, being visibly bent by the load attached at their free end. Since Ti-Ta experiences a thermoelastic martensitic transformation, during heating, achieved with a mobile burner, the specimens became austenitic (tougher) and lifted the load by work generating- shape memory effect (SME). During cooling, cause by water spraying, the specimens rebecame martensitic and lowered the load [14]. A multimeter with thermocouple was used to measure the temperature on specimen's surface. After

several tens of cycles, training was completed [15]. The specimens acquired a cold shape as a result of RT-bending. During subsequent heating they experienced free recovery SME, which was also observed at nonthermoelastic SMAs such as FeMnSiCr [16] or FeMnSiCrNi [17]. The evolution of specimen's free with temperature was recorded by cinematographic analysis [18].

Dynamic mechanical analysis (DMA) was performed, by means of a DMA 242 Artemis NETZSCH device using three-point bending specimen holder for characterizing flexural behaviour by temperature scans and strain sweeps. The temperature scans were performed between RT and 400°C, with force resolution of 0.0005 N, an amplitude of 20 μm and a frequency of 1 Hz. The strain sweeps were done at RT, with the frequency of 1 Hz and comprised five cycles during which amplitude increased from 0.1 to 20 μm , with an amplitude resolution: 0.0005 μm . Dynamic force was limited, by analyser's protection system, to 12 N and bending amplitude did no longer grow when this threshold value was reached due to dynamic work hardening. The DMA diagrams, recorded during temperature scans, display the variations of storage modulus (E') and internal friction (determined as the ratio between loss and storage modulus, $\tan \delta = E''/E'$), during a heating-cooling cycle. The diagrams recorded during RT strain sweeps reveal the variations of dynamic force with strain amplitude after removing the effect of the first cycle. Due to the dynamic character of the test the variation curves had to be smoothened by 6th degree polynomial fits, performed with Proteus software developed by NETZSCH [19].

By means of an experimental setup, the elasticity of 500 mm-long ribbons was evaluated by winding-unwinding tests, at RT. Tensile test were applied with an INSTRON 3382 tensile testing machine at a deformation rate of $2.77 \times 10^{-4} \text{ sec}^{-1}$.

3. Experimental results and discussion

3.1. Shape memory effect

The training procedure by SME cycles in bending is illustrated in figure 2.

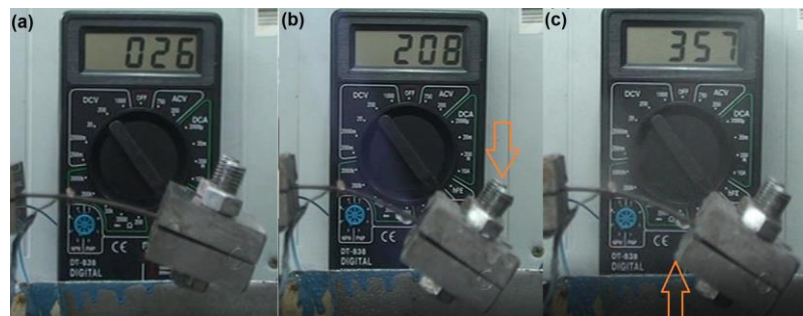


Figure 2. Training procedure by SME cycles in bending of a lamellar Ti-50 mass % Ta specimen: (a) cold shape of martensitic specimen, in initial state; (b) shape acquired after first heating-cooling cycle; (c) hot shape in austenitic shape at the end of second heating.

The specimen in cold rolled state, figure 2(a), has oriented martensite plates that are unable to support the 125-grams load fastened at its free end. This is why during the first heating, the specimen would lower the load. During subsequent cooling, thermoelastic martensitic transformation occurs and the specimen becomes even softer, as observed from figure 2(b). Therefore, during the first heating-cooling cycle the specimen will be lowered both during heating and cooling. It is this martensitic structure, obtained during *in situ* cooling under bending load the experiences reverse thermoelastic martensitic transformation and lifts the load by work generation SME, according to figure 2(c). At the end of the training procedure, the lamellar specimen acquired a bent cold shape, which is characterised by oriented martensite plates. When heated, this martensitic structure would reverse to austenite with partial deflection of macroscopic shape, by means of free-recovery SME, as illustrated in figure 3.

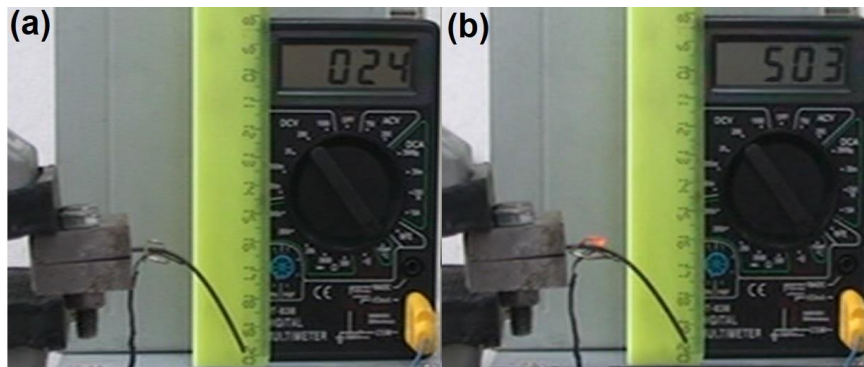


Figure 3. Illustration of free-recovery SME at the specimen trained in bending according to figure 2: (a) initial martensitic state; (b) final austenitic state.

The cold shape obviously became visibly bent in figure 3(a) while free-recovery SME caused a 2-mm lift of specimen's free end in figure 3(b). Figure 4 illustrates, by means of DMA thermograms, solution treatment effects on the variations of storage modulus and internal friction during heating.

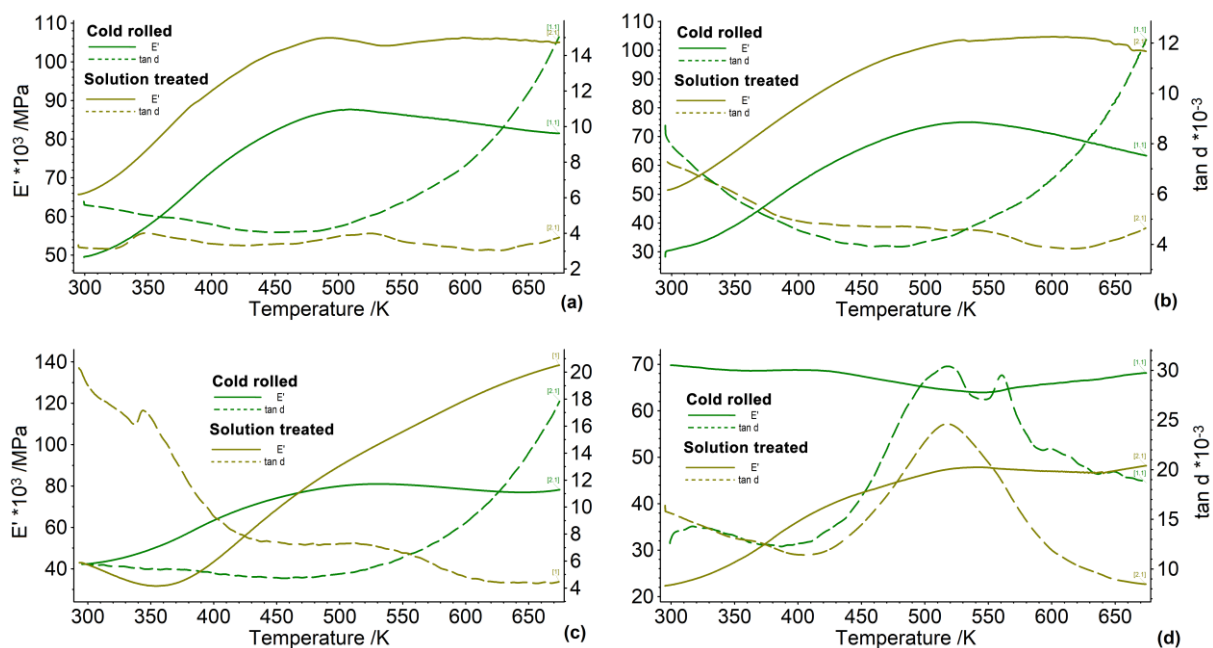


Figure 4. DMA thermograms recorded during heating: (a) 25Ta; (b) 30Ta; (c) 35Ta and (d) 50Ta.

The chemical composition effects are rather obvious when comparing the thermograms of specimens 25Ta, 30Ta and 35Ta with that of specimen 50Ta. The former three did not experience any solid state transition in cold rolled state, during heating, because internal friction ($\tan \delta$) did not reveal any maximum. This could be an effect of work hardening induced by cold rolling. During heating, internal stresses are relieved and storage modulus (E') typically doubles its value. Conversely, 50Ta reveals two internal friction maxima while storage modulus remains almost constant, around 70 GPa. After solution treatment, all of the four specimens experience a more or less obvious $\tan \delta$ maximum which are much more prominent at 50Ta. The presence of this pronounced internal friction maximum, observed at about 250°C at 50Ta specimen, in figure 4(d) illustrates a reverse martensitic transformation which is in good agreement with the occurrence of SME at this specimen, as shown in figures 2 and 3.

On the other hand, analysing the evolution of storage modulus with temperature at cold rolled and solution treated specimens, it appears that specimen 25Ta and 30Ta experienced rather similar phenomena characterized by an E' maximum at about 200°C. Storage modulus increased from cold rolled to solution treatment state, from 50 to 66 and from 30 to 51 GPa, respectively. Solution treatment effects, from the point of view of storage modulus variation, are quite different at specimens 35Ta and 50Ta. Thus, the former is much more sensitive to heating temperature, when in solution treated state while the latter seems to be less sensitive in cold rolled state. In addition, at 35Ta, both cold rolled and solution treated states had $E' \approx 42$ GPa, while at 50Ta E' decreased from 70 GPa at cold rolled state to 24 GPa at solution treated one.

3.2. Superelasticity

The presence of superelastic behaviour was first investigated by winding-unwinding tests. A 500 mm-long ribbon of cold rolled 30Ta was fixed at one end and wound four times for 360, 540, 720 and 900°, both to the right and to the left. The results are summarized in figure 5, where the values obtained after right-side winding loading and unloading are coloured in blue and designated by RL and Ru, while those for left-side winding are marked with red and the symbols LL and Lu, respectively.

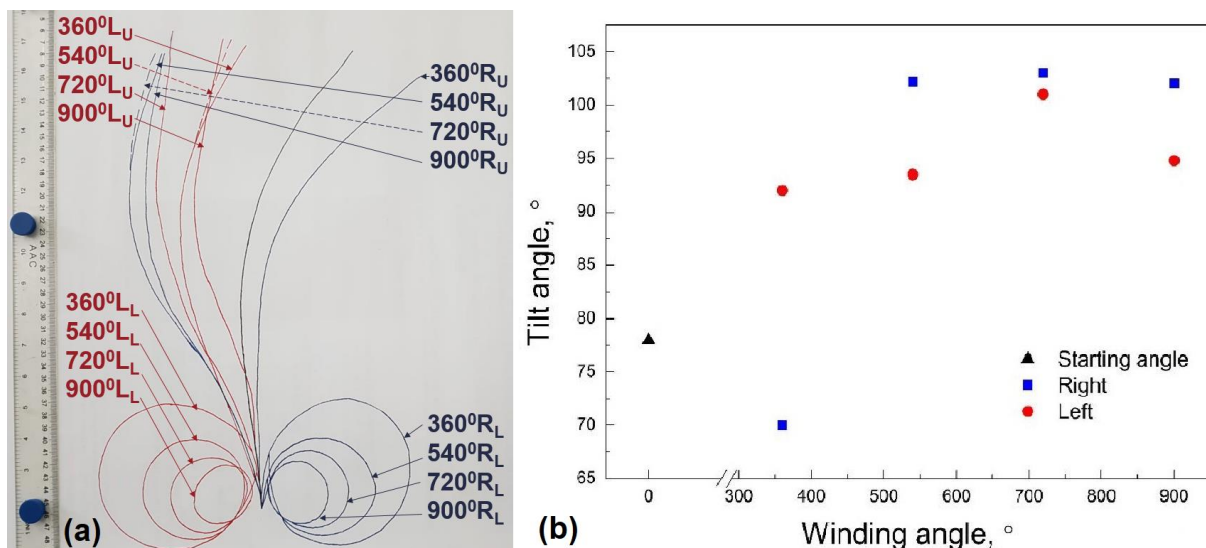


Figure 5. Emphasizing superelastic behaviour by winding-unwinding experiments performed on 500-mm long cold rolled 30Ta: (a) general view of the successive positions of the specimen; (b) variation of tilt angle as a function of the winding one.

The tilt angle was measured with a protractor between the position of the ribbon's free end and the white axis corresponding to 0°. It appears that the free-unwinding position reached a higher angle with increasing the winding angle. In any case, the ribbon sprung back to very similar positions, when wound between 540 and 900°, both on the right and on the left side.

In order to better evaluate superelastic behaviour, tensile tests were applied, firstly until failure, in order to determine the maximum stress, for subsequent mechanical cycling. The tensile failure stress-strain curves of the cold rolled specimens are summarized in figure 6 and the corresponding tensile parameters are summarized in table 1.

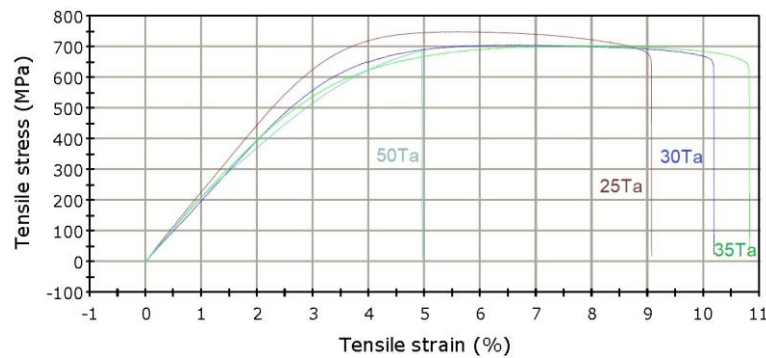


Figure 6. Tensile failure curves of cold rolled specimens.

Table 1. Summary of tensile parameters determined from the failure curves from figure 6.

Specimen	Yield stress (MPa)	Tensile strain at break (%)	Failure stress (MPa)	Modulus (GPa)
25Ta	638	9.1	748	21.8
30Ta	571	10.2	705	19.6
35Ta	509	10.8	701	19.2
50Ta	541	5.0	684	16.9

It is noticeable that the single monotonic variation tendency of tensile parameters, with increasing Ta amount, is to decrease for failure stress and elasticity modulus. When comparing the dynamic and static values of elasticity modulus determined at room temperature, from figure 4 and table 1, respectively, it is obvious that the former are much larger than the latter.

The tensile behaviour of specimen 25Ta in solution treated state, for 50 loading-unloading cycles to 400MPa, is shown in figure 7.

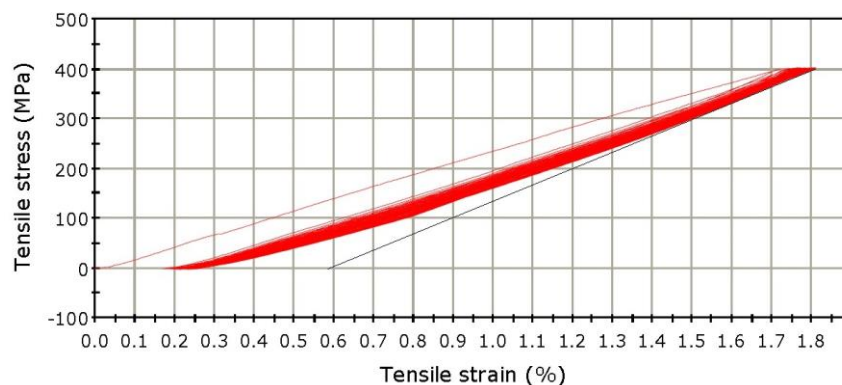


Figure 7. Stress-strain curves of 50 cycles applied to specimen 25Ta in solution treated state.

Maximum strain reached 1.81 % and permanent strain 0.25 %. This gives a recovery strain of 1.56 %. The intersect between the tangent to unloading curve and the abscissa has a strain of approx. 0.59 %. This means that elastic recovery strain is $1.81 - 0.59 \approx 1.22$ %. This leaves a difference of $1.56 - 1.22 \approx 0.34$ % which can be attributed to superelastic behaviour. The ratio between total and superelastic strain is $(0.34 / 1.81) \times 100 \approx 18.8$ %, a value which is close to that observed in other Fe base SMAs [20].

4. Conclusions

The results discussed above enable formulating the following conclusions:

- according to DMA thermograms recorded during heating, the alloys of Ti with 25, 30 and 35 mass % Ta did not experience any reverse thermally induced martensitic transformation, in cold rolled state, yet in solution treated state a diffuse transition is expected to occur;
- an obvious reverse martensitic transformation occurred in specimens with 50 mass %Ta in cold rolled condition and was amplified in solution treated state;
- the cold rolled 50Ta specimens weighing 1 g, developed work generating shape memory effect by lifting a 125-g load fastened at their free end as well as free-recovery SME;
- a 500-mm long cold rolled 30Ta ribbons experienced a superelastic behaviour during winding-unwinding tests by adopting very same positions after being winded between 540 and 900⁰, both on the right and on the left side;
- increasing Ta amount caused monotonic decreases of both failure stress and elastic modulus;
- during 50 tensile loading-unloading cycles the solution treated specimens containing 25 mass % Ta developed a stabilized behaviour characterized by superelastic strains above 18 %;
- additional investigations are necessary in order to evaluate ageing with solution treatment effects on thermal and mechanical memory responses of Ti-Ta shape memory alloys and to corroborate the results with chemical composition effects.

5. References

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