On the functional degradation of binary titanium–tantalum high-temperature shape memory alloys — A new concept for fatigue life extension

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High-temperature shape memory alloys are promising candidates for actuator applications at elevated temperatures. Ternary nickel–titanium-based alloys either contain noble metals which are very expensive, or suffer from poor workability. Titanium–tantalum shape memory alloys represent a promising alternative if one can avoid the cyclic degradation due to the formation of the omega phase. The current study investigates the functional fatigue behavior of Ti–Ta and introduces a new concept providing for pronounced fatigue life extension.

Keywords: Omega phase; martensite; phase transformation; microstructure; shape memory effect.

Conventional shape memory alloys (SMAs) have been intensely investigated over the last decades due to their extraordinary properties.^{1–6} Different metallic alloys can show a shape memory effect, e.g. Cu-based⁵ and Fe-based systems,⁶ but Ni–Ti is still the most widely used conventional SMA³ due to good functional and structural properties. Unfortunately, the transformation temperatures of Ni–Ti are limited to below 100°C, thus hindering applications in elevated and high-temperature regimes.⁷ As shape memory actuators allow for designing devices characterized by high compactness and efficiency, a large effort has been spent to develop high-temperature shape memory alloys (HTSMAs). For actuation in a medium temperature range of about 100–400°C, mainly Ni–Ti based ternary (Ni–Ti–X) systems have been proposed.^{8–10} These alloys show promising shape memory characteristics, i.e. actuation strain and microstructural stability, but at the same time suffer from two main drawbacks, i.e. poor workability and/or high amounts of noble metals.^{8,9,11}

Titanium–tantalum SMAs represent a promising alternative to overcome all these issues if one can avoid the cyclic degradation due to the formation of the ω -phase. The current

study investigates the functional fatigue behavior of Ti–Ta and introduces a new concept providing pronounced fatigue life extension. The cyclic deformation behavior of a polycrystalline titanium–tantalum (Ti–Ta) alloy containing 30 at.% Ta under iso-stress loading during thermal cycling employing temperatures ranging from 50°C to 600°C was investigated. In order to reveal the most detrimental factor leading to a change of transformation temperatures and a loss of transformation strain, fatigue tests were conducted with differing heating and cooling rates and aging treatments. Using X-ray diffraction (XRD) it could be clearly shown that stabilization of the high-temperature parent phase (β -phase) and the concomitant evolution of the ω -phase led to functional degradation. The results of the current study suggest that both phases are mainly induced through aging during high temperature exposure and not by martensitic transformation events during cycling. A new concept employing single-step short-time annealing for regeneration of the initial transformation behavior is introduced.

As shown and intensively discussed in a series of studies published by Buenconsejo *et al.*,^{12–14} the Ti–Ta system is characterized by relatively cheap alloying elements and excellent workability. It thus complies with demands of robust industrial applications. However, it has also been revealed

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that binary Ti–Ta alloys lack functional stability.^{12–14} This is attributed primarily to the formation of the ω -phase, which is known to form in similar alloys like Ti–Nb, for example.¹² Concomitant, the high-temperature parent β -phase in Ti–Ta alloys is stabilized down to lower temperatures and consequently hinders the shape memory effect.^{12–14} Ternary elements allow for improvement by delaying the formation of the ω -phase, thus stabilizing the shape memory effect and its cycling behavior investigated up to 20 cycles.^{13,14} As functional fatigue and microstructural evolution are crucial factors for a sound understanding of the alloy performance, the current study addresses these issues, by employing heating and cooling rates differing by a factor of 75 in tests conducted at temperatures up to 600°C for up to 500 cycles. Microstructure analyses were performed to uncover the factors that govern functional degradation. Finally, a heat treatment process was established that leads to restoration of the initial properties eventually allowing for substantial fatigue life extension.

In the current study, dogbone-shaped tensile specimens with a nominal gauge length of 55 mm and a cross section of 1.5 mm × 1.0 mm were prepared from polycrystalline Ti–Ta sheet material with 30 at.% Ta using electro-discharge machining (EDM). The Ti–Ta alloy was produced using high-purity Ti and Ta as raw materials for arc melting. After homogenization, annealing sheets were produced by rolling. The final recrystallization annealing was carried out at 900°C for 10 min. The details on alloy preparation and processing are given elsewhere.¹⁵ The tensile samples were mechanically ground in order to remove surface layers resulting from EDM. For phase analyses and mechanical testing, the samples were mechanically ground down to a grit size of 5 μ m followed by vibro-polishing. The fatigue tests were carried out using a servo-hydraulic test rig. Tests were conducted under stress control employing loads ranging from 0 to 200 MPa. An induction heater was used for heating and temperatures were controlled using thermocouples which were fixed onto sample surfaces. In order to avoid any structural change, e.g. induced by spot welding, a thin copper wire was wound around the sample and the thermocouple in such a way that proper contact was ensured. Temperatures as well as thermal gradients were cross-checked by thermal imaging. The temperature gradient within the gauge length was always below 5°C. Using this setup, heating rates of 0.33°C s^{−1} and 25°C s^{−1} were employed. Forced cooling was realized using compressed air. For the aging procedures, the samples were heated either load free in a conventional furnace or under a given mechanical load in the test rig. Pre- and post-fatigue phase analyses were done using XRD using a Cu-K α -source operating at 45 kV and 40 mA. For all XRD measurements, the sample surfaces were prepared as described above.

Fig. 1. Strain–temperature curves at heating rates of 25°C s^{−1} for Ti–30Ta. Transformation strain becomes noticeable at a stress level of 50 MPa, and higher residual strains can be observed above 150 MPa.

Figure 1 shows strain–temperature curves for Ti–30Ta under different superimposed stresses. The curves are plotted with respect to relative strain. The tests were conducted in stress control with stress levels ranging from 0–200 MPa. At a low load level of 50 MPa, transformation strains are small. Transformation strains significantly increase at higher load levels, but for loads above 100 MPa, the presence of irreversible strains is clearly revealed. Consequently, all tests conducted in the remainder of this study were conducted at 100 MPa, as this is the optimum value with respect to transformation strain and reversibility of the martensitic transformation. In the following tests, the effects of different heating and cooling rates at a constant load level of 100 MPa were considered. As has been described before, these rates differ by a factor of 75. Two sets of data are shown in Fig. 2. Figure 2(a) details the results employing slow heating/cooling rates (which are similar to those of the work of Buenconsejo *et al.*¹²).

As has been found previously,¹² a rapid decrease of transformation temperatures can be found in the early stages of cycling. Buenconsejo *et al.* attributed this to the formation of the ω -phase,^{12–14} which seems to evolve in the current material as well, as will be shown later. As can be deduced from Fig. 2(a), the current alloy almost fully lost its shape memory effect in the fourth cycle. This loss of functionality is well known for similar SMAs, e.g. Ti–Nb.¹² As can be seen in Fig. 2(b) the evolution of transformation temperatures and transformation strains is qualitatively similar when heating and cooling rates are increased by a factor of 75. It is important to note, however, that cycle numbers 1 to 500 are plotted in Fig. 2(b). Consequently, the number of cycles itself is not a key factor for the degradation behavior in Ti–Ta HTSMA, in contrast to what is known for other SMAs, e.g. Ni–Ti. Investigating the aging behavior in an interval ranging from 250°C to 700°C, it is revealed that aging at temperatures in between 250°C and 400°C leads to a significant drop of the martensite

Fig. 2. Cyclic strain–temperature curves obtained for Ti–30Ta at heating rates of (a) $0.33^{\circ}\text{C s}^{-1}$ and (b) $25^{\circ}\text{C s}^{-1}$.

start temperature (M_S). This is caused by the formation of the ω -phase.^{12,15} Thus, the dwell time in the *critical* temperature regime, i.e. from 250°C to 400°C for the tests conducted in the current study, can be calculated for the curves shown in Fig. 2. For the rate of $0.33^{\circ}\text{C s}^{-1}$, the dwell time is 15 min for each thermal cycle. For the higher rate the dwell time was found to be 12 s for a single cycle, which corresponds to 20 min when considering 100 heating–cooling cycles.

In order to reveal the effect of dwell time, additional tests have been conducted employing artificial aging following the first thermomechanical cycle. Figure 3 shows the effects of both, cycling and constant temperature aging, on the strain–temperature curves. The first cycle of the initial material state (Fig. 3 lower part) corresponds to what is observed for the as-processed Ti–Ta, Fig. 1. Next, the specimen was aged at 350°C for 20 min under a constant load of 100 MPa. The parameters have been chosen based on the critical

temperature range and dwell times discussed above. The first cycle following this heat treatment (Fig. 3 right-hand side) shows a strain–temperature curve which is similar to the curve obtained after fatigue for 100 cycles, employing the high heating rate shown in Figs. 2 and 3 (left-hand side). For both conditions, martensite start temperatures (indicated by arrows in Fig. 3), and transformation strains are strongly affected. In comparison to the samples that were exposed to thermomechanical cycling, functional degradation seems to evolve slightly faster in the aging experiment. Consequently, the ω -phase formation is almost solely influenced by the dwell time in a critical temperature range with the most detrimental temperatures being around 350°C . Buenconsejo *et al.* report similar trends following aging, but in their study they conducted aging at lower temperatures using a Ti–Ta alloy with a different composition.¹²

In a subsequent step, the samples have been heat treated at a higher temperature of 600°C for very short times, i.e. ranging from 1 to 5 min. This type of short time treatment has been proposed for functional optimization of Ti–Nb alloys, but that case was aiming at property optimization with respect to superelasticity at room temperature.^{16,17} In the current study, the heat treatment of the Ti–Ta samples was performed with a different objective in mind. As shown in Fig. 3 (upper part), the functionally degraded specimens fully recover their initial transformation strain ability of about 1%. Concurrently, M_S is shifted toward its initial value, i.e. to higher temperatures. The same finding was obtained for all other degraded conditions, i.e. irrespective of the heating rate used (c.f. Fig. 2). The minor differences in hysteresis shape are currently under investigation. The recovery of the functional properties eventually will allow for substantial extension of the fatigue life of Ti–Ta HTSMAs.

For better understanding of microstructure evolution upon aging and recovery treatment, XRD phase analyses were carried out at room temperature. Results for representative

Fig. 3. Strain–temperature curves for Ti–30Ta following different treatments. The initial cycles shown at the bottom depict the behavior of the as-processed condition. Evolution of M_S is schematically indicated by the bold gray arrows. Following 100 cycles and 20 min artificial aging the transformation strain is very similar indicating the dominant effect of dwell time. Concurrently, M_S is shifted to a lower value in the aged Ti–Ta. Through short time recovery treatment strain capability and M_S are restored as shown by the curves in the upper part of the diagram.

Fig. 4. XRD profiles showing relative intensities at room temperature for Ti-30Ta in different conditions. The as-processed condition and the condition following recovery treatment depict a martensitic state, whereas the artificially aged condition is characterized by high intensity peaks from the β -phase.

samples from Figs. 2 and 3 are shown in Fig. 4. The as-processed Ti-Ta is characterized by a fully martensitic α'' microstructure in accordance with data from literature.¹² Irrespective of the actual fatigue testing procedure, i.e. thermal cycling or artificial aging in the critical temperature regime, the microstructure changed in a similar way. The presence of the ω -phase can be revealed for all thermally loaded specimens, but due to the small volume fraction of the ω -phase particles, the intensity of the peaks remains small. In addition, the β -phase is stabilized in all fatigued samples. The similarity of the XRD diffractograms suggests a similar microstructural evolution in all specimens. As a consequence of β -phase stabilization, the Ti-Ta samples tested under different loading sequences degrade and eventually lose their functionality. Clearly, such kind of microstructural and functional degradation needs to be kept at a minimum for applications of Ti-Ta HTSMA. As has already been shown by Buenconsejo *et al.* ternary elements, e.g. aluminum and tin, are suitable means to hamper ω -phase formation.^{13,14} Using short time recovery, the current study introduces an alternative approach for property optimization, especially with respect to fatigue life extension. The concept can be easily implemented in actuator applications. The short time recovery treatment results in restoration of the initial transformation strain capability. The effect of the short time recovery annealing is attributed to dissolution of ω -phase, which eventually resets β -phase stabilization.

The functional fatigue behavior of a binary Ti-Ta alloy was investigated in the current study. By employing different testing parameters, new insights into the mechanisms governing the cyclic degradation of Ti-Ta HTSMA were

obtained. Especially the influence of heating-cooling rates and dwell times in a critical temperature interval has been revealed. In addition, a recovery treatment has been proposed leading to significant fatigue life extension.

The main conclusions from the results obtained in the present work can be summarized as follows:

- (1) Cyclic degradation of Ti-Ta HTSMAs is due to ω -phase formation and stabilization of the β -parent-phase.
- (2) The most important factor for degradation of the Ti-Ta binary alloy is the dwell time spent in the temperature window ranging from about 250°C to 400°C. This is due to intense ω -phase formation occurring exclusively in this region.
- (3) A short time annealing at a temperature of 600°C allows for full restoration of the initial transformation strain capability of the Ti-Ta binary alloy.

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