Executive Summary

The present study contributes to a better understanding of microstructural evolution in binary Ti-Ta-based high-temperature shape memory alloys (HT-SMAs) through different thermal and thermo-mechanical treatments. Ti-Ta alloys are considered for application as actuators for example in aerospace industries due to their martensite start temperatures, which can surpass 200°C and are thus significantly higher compared to Ni-Ti alloys. Thermal investigations using differential scanning calorimetry (DSC) as well as scanning and transmission electron microscopy (SEM and TEM) were carried out to investigate the microstructure and thermal phase transformation behavior. It is already known that binary Ti-Ta HT-SMAs suffer from degradation of functional properties, such as phase transformation temperatures (PTT). A strong decrease of the PTTs occurs e.g. during aging of Ti-Ta alloys in a temperature range from 100°C to 400°C due to the formation of the hexagonal ω-phase.

The first part of the present work deals with DSC investigations of binary Ti-Ta HT-SMAs in order to obtain DSC data for the PTT. Sheets of binary Ti-Ta were produced using vacuum arc melting (VAM). The ingots were homogenized at 1100°C for 25 hours with subsequent water quenching (WQ) and afterwards cold rolled to a deformation level of around 90 %. Recrystallization treatments were performed either at 800°C or 900°C for 10 minutes with subsequent water quenching. Using the line intersection method, the mean grain size was determined as 8 µm and 14 µm, respectively. Ti-Ta alloys with different chemical compositions and different sampling points of the cold rolled and recrystallized sheets were analyzed using DSC. It was found that the PTT decreased by approximately 20°C per addition of 1 at.-% Ta. For Ti$_{70}$Ta$_{30}$ the martensite-start-temperature ($M_s$) is 173°C and the austenite-finish-temperature ($A_f$) is 213°C. The homogeneity of the specimens is shown by the fact that the PTT is not affected by the sampling locations of the DSC specimens along the longitudinal or transverse axis of a Ti$_{70}$Ta$_{30}$ sheet. As expected from DSC measurements, TEM investigations at room temperature reveal a martensitic orthorhombic α”-microstructure of the sheets recrystallized at both 800°C and 900°C.

The second part of this work deals with aging heat treatments and both thermal and thermo-mechanical cycling experiments of binary Ti-Ta alloys. Aging treatments of the Ti$_{70}$Ta$_{30}$ sheets at 300°C for 30 minutes or 4 hours lead to the formation of the hexagonal ω-phase inside a body-centered cubic (bcc) β-phase matrix and to the suppression of the phase
transformation peaks as determined by DSC. After aging for 4 hours a separation of Ti- and Ta-rich regions at grain boundaries occurs.

Thermal cycling of Ti<sub>70</sub>Ta<sub>30</sub> sheets in a temperature range from 20°C to 300°C with a heating and cooling rate of 20°C/min leads to a shift of the PTTs to lower temperatures after each thermal cycle and a flattening of phase transformation peaks. After 5 thermal cycles, the martensitic transformation is more or less suppressed. Based on TEM investigations and selected area diffraction (SAD) analysis the reason for the degradation of the shape memory effect (SME) can be identified as the formation of the hexagonal ω-phase. SAD analysis reveals that after 5 thermal cycles of a Ti<sub>70</sub>Ta<sub>30</sub> sheet, the microstructure consists of a mixture of bcc β-phase matrix, α’-martensite and ω-phase. The same mixture of phases was observed after thermo-mechanical cycling. The Ti<sub>70</sub>Ta<sub>30</sub> sample was cycled 12 times in a temperature range from 30°C to 400°C under a load of 100 MPa with a heating rate of 40°C/min. Additionally, a degradation of the SME in a Ti<sub>67</sub>Ta<sub>33</sub> thin film was observed after cantilever testing (thermo-mechanical cycling). In the initial as-deposited state, the Ti<sub>67</sub>Ta<sub>33</sub> thin film shows a columnar structure with a longitudinal axis perpendicular to {120} or {102} planes. After cantilever testing, a columnar structure was still observed. In SAD analysis it was found that the microstructure was then austenitic (bcc β-phase) and ω-phase was present.

The third part of this thesis focuses on creep investigations of a Ti<sub>70</sub>Ta<sub>30</sub> alloy and microstructural changes due to creep exposure and after stress-free aging under creep conditions. Miniature creep specimens were tested in an Ar atmosphere in a temperature range between 470°C and 530°C and at stresses ranging from 90 to 150 MPa. Analysis of the creep data yields a stress exponent <i>n</i> of 3.7 and an activation energy for creep <i>Q_{eff}</i> of 307 kJ/mol. Both creep exposure and stress-free aging lead to a full suppression of the SME in Ti<sub>70</sub>Ta<sub>30</sub>, which was further confirmed using DSC. SEM and TEM investigations reveal that a strong unmixing of the solid solution matrix occurs during creep and aging. The severe degradation of the SME is probably related to this phase separation. At grain boundaries Ti- and Ta-rich precipitates formed. The Ti-rich precipitates contain around 95 at.-% Ti and with TEM SAD analysis they were found to be hexagonal (α-phase). The Ta-rich precipitates contain 65 at.-% Ta and exhibit a bcc β-phase structure. Inside the austenitic β-phase grains (~ 56 at.-% Ti) decomposition leads to the formation of plate shaped Ti-rich (~ 94 at.-% Ti) precipitates with bcc structure.

The technical application of Ti-Ta alloys is currently limited by the strong tendency to ω-formation on aging and thermal cycling and the tendency to phase separation during creep and aging. Further work is necessary to overcome these limitations.