Ti-Ta High Temperature Shape Memory Alloys

G Chilnicean*, A Novac, R Sprincenatu, V Bolocan and C Craciunescu

Department of Materials and Manufacturing Engineering, Faculty of Mechanical Engineering, Politehnica University Timisoara, Bd. Mihai Viteazul 1, 300006 Timisoara, Romania

*Corresponding author: george.chilnicean@yahoo.com,

Abstract. The actuation based on shape memory alloys relies on the martensitic phase transformation that allows the reversible transition from the “soft” martensite phase to the “hard” austenite phase. Usual shape memory alloys usually have transformation temperatures around room temperature. While these are suitable for biomedical devices a higher temperature range is needed for applications that are designed to work in aerospace applications. High temperature shape memory alloys belonging to the Ti-Ta system manufactured by arc melting are investigated for their potential to be used in applications requiring the actuation based on martensitic transformation. The microstructure is analyzed based on X-ray diffraction and scanning electron microscopy whereas the martensitic transformation is investigated based on differential scanning calorimetry experiments.

1. Introduction
The shape memory effect was observed on numerous alloy systems, among which the so-called Ni-free alloys, based on Ti (like Ti-Ta, Ti-Mo, Ti-Nb) are ones that can provide a large range of transformation temperatures for a variation of the composition [1-4].

A number of applications requiring high temperature actuation cannot use the typical shape memory alloys because their actuation temperatures are limited to about 100 °C. Hot environments like the one required by home appliances, automotive or aerospace industry or power generation systems need significantly higher transformation temperatures.

Among the high temperatures shape memory alloys (HTSMA) the Ti-X (X=Pd, Au, Zn) and Ru-X (X=Nb, Ta) are the ones capable of leading to Ms transformation temperatures above 400 °C [5-8]. The β-type Ti-base alloys can show interesting shape memory and associated properties (like superelasticity and shape memory properties by taking advantage of the β→α" reversible martensitic transformation. The parent β-phase in Ti alloys is obtained by stabilization via the addition of β stabilizing elements. Tantalum is a stabilizing element that also has the potential to increase the martensitic transformation temperature and to limit the formation of the ω phase during aging at intermediate temperatures, a phase that can suppress the martensitic transformation [9].

The fabrication and microstructure of a Ti-Ta alloy was investigated in this paper in order to develop the shape memory alloys with higher transformation temperatures.

2. Experimental details
Ti-Ta alloys have been manufactured by arc melting technique using an Arcmelter equipment (Edmund Bühler GmbH), in Ar atmosphere, after the chamber was high-vacuumed to 3x10-5 mbar. Several re-melting were made to ensure the homogeneity of the resulting alloys. Heat treatments were
performed for samples transversally cut from the as-cast buttons encapsulated in quartz tubes vacuumed at 3x10⁻⁵ mbar and sealed. The samples were heated at 1000 °C and maintained for 36 ks, followed by furnace cooling. Further on the vacuum sealed samples were heated at 900 °C and quenched in room temperature water by breaking the quartz tube in water.

Structural analysis was performed by X-ray diffraction in an X’Pert³ Powder (PANalytical) at room temperature. Monochromatic Cu Kα was used as radiation, with a 1.541840 Å wavelength, 40 mA power at 40 KV, 0.04 mm step with a 0.5 s/step, for a 20° – 90° 2θ range. Microstructural observations of the samples was made by scanning electron microscopy (SEM) in a TESCAN Vega 3 LM scanning electron microscope (SEM), equipped with a Bruker Quantax 200 Energy Dispersive X-ray Spectroscopy (EDX) system with Peltier-cooled XFlash 410M silicon drift detector.

3. Experimental results
The buttons made out of Ti-Ta alloys by arc melting showed a relatively good homogeneity following seven to eight re-melting and homogenization annealing. An analysis of the phase diagram corroborated with the EDS investigation of the composition of the alloy recorded on a sample cut from the button is shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** Analysis of the alloy composition based on the phase diagram and the EDS results.

(Ti-Ta phase diagram after Phase Diagrams of Binary Titanium Alloys, 1987).

The composition of the alloy falls in the range where the shape memory effect was reported for the Ti-Ta system. The microstructural observation of the free-solidification part of the as-cast button (figure 2) shows a dendritic structure (with dendrites and interdendritic spaces), typical for Ti-alloys [9]. According to the phase diagram (figure 1) an α+β structure is expected to be present at room temperature over a large compositional range in the as-cast alloy. Further EDS investigations showed that the solidification surface is Ti-rich, indicating that the Ti tends to segregate during the solidification process.
a) View of the as-cast solidification surface  

b) Area with denidritic structure

**Figure 2.** Microstructural aspects of the as-cast surface.

The martensitic transformation that appears in Ti-Ta shape memory alloy is influenced by the composition, with the Ms temperature tending to reach temperatures lower than room temperature for compositions with Ta content higher than 40%. Buttons quenched were analyzed by electron microscopy and X-ray diffraction.

The Ti-rich as-cast surface of the button shows after quenching a lamellar structure which appears to be influenced by the pre-existing dendritic structure and is of limited interest for the shape memory properties.

**Figure 3.** Detailed microstructural aspects of the as-cast surface.

**Figure 4.** XRD profile of the Ti-Ta alloy solution treated at 900 °C and water quenched.

The quenching of the alloy leads to the formation of a martensite structure that identified in the X-ray spectra shown in figure 4. The structure is composed of α" martensite that was stabilized at room temperature by quenching and has an orthorombic crystal structure, which is consistent with the data reported in literature.
The presence of the martensite in the microstructure is a premise for the existence of shape memory properties in the alloy.

4. Conclusions
The structure of a Ti-Ta alloy analyzed in the as-cast and quenched state reveals the formation of a martensitic structure following quenching from 900°C in water. The corresponding martensite is α″ orthorhombic as it resulted from the X-ray diffraction profile.

A segregation of Ti-rich phase was observed on the surface of the as cast sample, thus several remelting are needed in order to obtain a homogenous composition throughout the thickness of the arc melted button.

5. References
[1] Kim H S, Kim W Y and Lim S H, 2006 Scripta Mater. 54 887.
[2] Ping D H, Mitarai Y and Yin Y X, 2005 Scripta Mater. 52 1287.
[3] Kim J I, Kim H Y, Hosoda H and Miyazaki S, 2005 Materials Transactions. 46 852.
[4] Kim H Y, Hashimoto S, Kim J I, Inamura T, Hosoda H and Miyazaki S, 2006 Mater. Sci. Eng. A 417 120
[5] Yamabe-Mitarai Y, Arockiakumar R, Wadood A, Suresh K S, Kitashima T, Hara T, Shimojo M, Tasaki W, Takahashi M, Takahashi S and Hosoda H, 2015 Materials Today: Proceedings 2S S517
[6] Shinohara Y, Tahara M, Inamura T and Miyazaki S, 2015 Materials Transactions 56(3) 404.
[7] Xue D et al. 2016 Sci. Rep. 6, 28244; doi: 10.1038/srep28244
[8] Abdul Wadood and Yoko Yamabe-Mitarai, 2014 Materials Science and Engineering: A 601 106
[9] He G, Eckert J, Löser W and Schultz L, 2003 Nature Materials 2 33

Acknowledgements
The authors acknowledge the support through the PIRSES-GA-2013-612585-MIDAS International Research Staff Exchange Grant of the PEOPLEMARIE CURIE ACTIONSFP7-PEOPLE-2011-IRSES. Equipment for experiments acquired through the Romania-Republic of Serbia IPA Cross-border Cooperation Programme, Project MIS ETC no 1328 “Pole of Collaboration in New Functional Alloys”.

Figure 5. SEM image of the Ti-Ta alloy following quenching (center of the cross sectional sample).