ESRF	**Experiment title:** Thermal decomposition pathways and competing precipitation reactions in martensitic TiNb alloys	**Experiment number**: HC- 1454
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Report:

β-stablized Ti-based alloys combine a series of advantageous properties that render them attractive for various kinds of biomedical implant applications. While their relatively low elastic modulus is beneficial for load-bearing components, the reversible martensitic transformation between the high-temperatur β-phase and the martensite α'' is the basis for shape memory and superelastic behaviour.

The microstructures of β-stabilized Ti-based alloys very strongly depend on the thermal history, which is particularly true for the Ti-Nb alloy family. The thermal decomposition of martensitic Ti-Nb alloys above room temperature is characterized by complex and diverse transformation, respectively precipitation pathways. This complexity results from the occurrence of simultaneous phase reactions. Knowledge of these thermal instabilities and precipitation sequences in these alloys is essential to develop processing schemes for Ti-Nb based shape memory/superelastic materials and structural components with predictable mechanical behaviour. The use of synchrotron X-ray diffraction at the beamline ID11 of the ESRF allowed *direct* observation of the phase transformatons during thermal cycling in-situ and to gain detailed knowledge about the evolution of phases.

Five binary Ti-Nb alloys with Nb contents ranging from 16 – 36.5 wt.% were chosen for this study . The samples were thin rods, about 900 µm in diameter, which had been solution treated in the single β-phase field and quenched into water at room temperature in order to prepare the martensitic state. Additionally, a sample of Ti-16.1Nb, which had been processed by high pressure torsion (HPT) beforehand, was heated in-situ in order to study the thermal decomposition of HPT-induced ω-phase [1]. The experiments were conducted at the ID11 materials science beamline. A resistively heated Linkam hot stage was used to thermally cycle the samples with heating and cooling rates of 10°C/min. The beam had an energy of 60 kV and a cross-section of 50x50 µm^2. Diffraction patterns were recorded by a 2D detector measuring with 2048x2048 pixels, an acquisition rate of one pattern per °C and an exposure time of 0.2 s. Background subtraction and azimuthal integration of the 2D patterns was performed with Fit2D.

A brief overview of the results is given below, where particular emphasis is placed on the alloys Ti-21.5Nb and Ti-29Nb. Figure 1 shows the 1-dimensional diffraction patterns of the alloy Ti-21.5Nb between 350°C

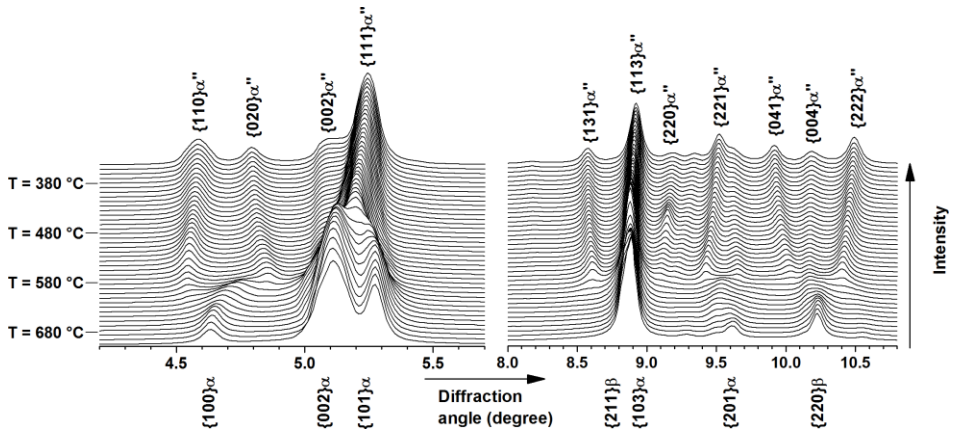

Figure 1: 1-dimensional diffraction patterns obtained during heating of Ti-21.5Nb with 10°C/min.

and 700°C. At room temperature this alloy exhibited a martensitic microstructure consisting of orthorhombic α''. Heating causes the lattice parameters of α'' to change, as evidenced by the shifts in the reflex positions. Differential scanning calorimetry (DSC) revealed a prominent exothermic reaction between 500°C and 600°C on heating (not shown here). The in-situ X-ray diffraction patterns (Fig. 1) show that in this temperature range the intensities of the martensite reflections decreased while reflections corresponding to α- and β-phases appeared. Hence, it can be concluded that reversion of martensite to austenite β did not take place, but instead at around 560°C the martensite α'' became thermally unstable resulting in the precipitation of α- and β-phases. A different behaviour was revealed in Ti-29Nb. Figure 2 presents the 1-dimensional diffraction patterns of the alloy Ti-29Nb between 290°C and 380°C. In contrast to Ti-21.5Nb, heating DSC measurements of this alloy in this temperature range exhibited an endothermic reaction which was immediately followed by a strong exothermic reaction. The corresponding diffraction patterns (Fig. 2) show a decrease of the volume fraction of α'' that is followed by the appearance of β- and ω-phases. The endothermic nature evidences that α'' martensite reverts displacively back to austenite β, instead of decomposing diffusionally as observed in Ti-21.5Nb.

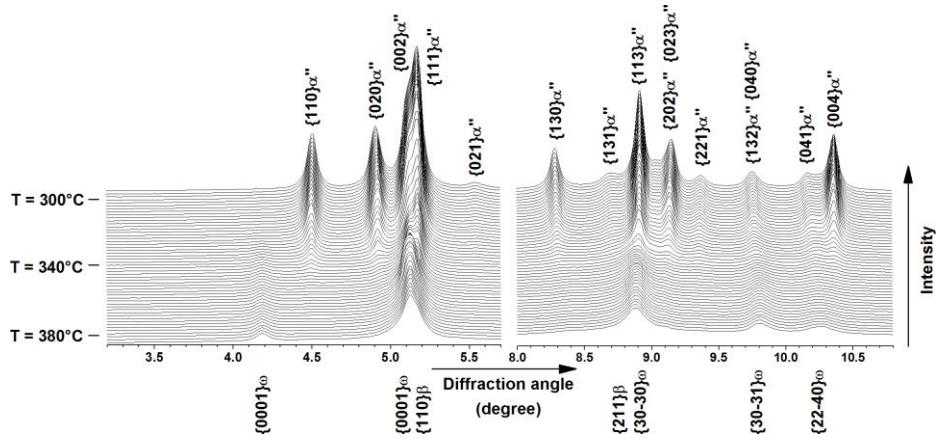

Figure 2: 1-dimensional diffraction patterns obtained during heating of Ti-29Nb with 10°C/min.

In a similar manner, the evolution of phases observed by in-situ diffraction in the remaining alloys was coupled to DSC measurements. Furthermore, the unit cell parameters were extracted from the patterns as function of temperature. The obtained results are not presented here at this point due to the limited space. In summary, the use of in-situ X-ray diffraction during thermal cycling enabled to clearly identify phase reactions observed by DSC and allowed establishment of thermally induced phase transformation sequences in martensitic Ti-Nb alloys. These results will contribute to the development of new heat treatment protocols for Ti-Nb-based alloys.

[1] A. Panigrahi, M. Bönisch, T. Waitz, M. Calin, W. Skrotzki, J. Eckert, M.J. Zehetbauer: Thermal stability of HPT-induced omega phase in biocompatible Ti-16.1Nb alloys Proceedings of the 7th International Conference on Solid-Solid Phase Transformations in Inorganic Materials (PTM) 2015, TMS USA, 263-268