Crystallographic Phases of NiTi Scaffolds Fabricated by Selective Laser Melting

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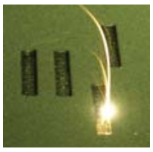
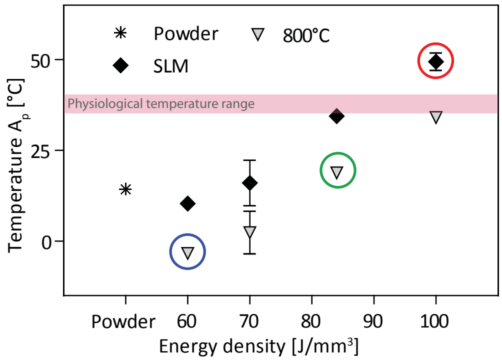
INTRODUCTION



NiTi - an FDA-approved material - belongs to the shape memory alloys (SMA) which exhibit superelasticity, shape memory effects and damping properties. The effects occur in the physiological temperature range and are therefore successfully applied in biomedical applications, e.g. in self expanding stents. By the additive manufacturing technique of selective laser melting (SLM), specimens with complex geometries and shape memory properties have been produced. Furthermore, we used SLM to fabricate NiTi parts with different phase transition temperatures.[2] The specimens have been characterized by X-ray diffraction to identify the crystallographic phases at different temperatures. We are going to realize complex shaped implants with sophisticated performance based on properties tailored within the SLM fabrication process.

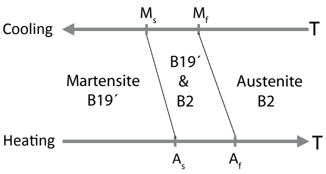
MATERIAL & METHODS

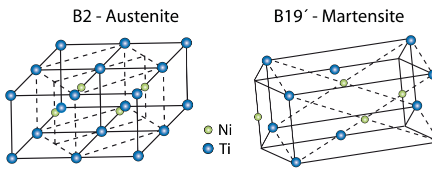
NiTi-specimens were manufactured by SLM from NiTi-powder (MEMRY GmbH, Weil am Rhein, Germany) using the SLM Realizer 100 (SLM-Solutions, Lübeck, Germany). Phase transition temperatures were tailored during the SLM fabrication process with varied energy densities and solution annealing at 800 °C. All processing steps were carried out under Ar atmosphere to protect the material from oxidation. The samples used in the presented investigations have austenite peak temperatures A_p of -3 °C (Sample 1), 50 °C (Sample 2) and 20 °C (Sample 3). Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements were accomplished at NiTi-powder and the specimens. XRD investigations were conducted at 34 °C.



PHASE TRANSITION

The shape memory effect and the superelasticity are caused by martensitic phase transitions. Upon cooling below the martensite start temperature M_s the parental high temperature austenite phase (B2) starts to transform into the low temperature martensite phase (B19´). The phase transformation is terminated at the martensite finish temperature M_f. Upon heating, a hysteresis of the austenite transformation temperatures takes place. The transformation does not involve atomic diffusion but a shearing of the crystal lattice.



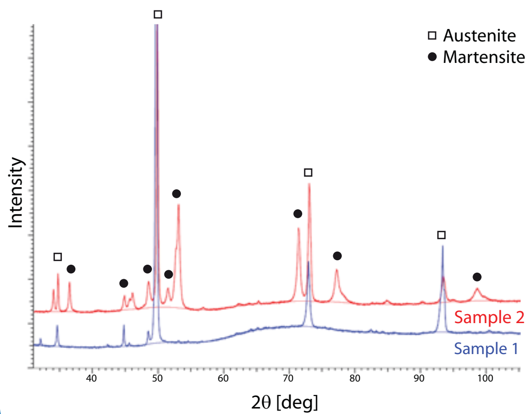


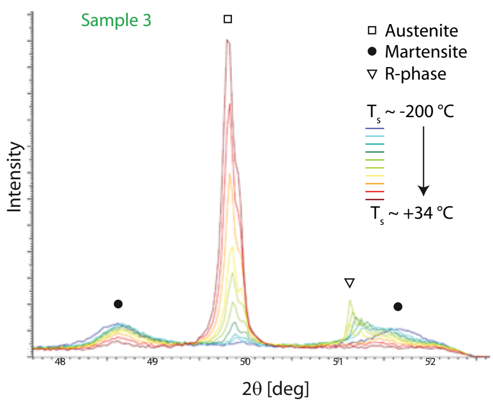
Besides the one step phase transformation (B2 ↔ B19´), a two step transformation can take place. In this case, the phase transformation involves a third NiTi-phase, the so called R-phase. The R-phase appears between the austenite and the martensite phase upon cooling or upon cooling and heating.[4]

X-RAY DIFFRACTION

As seen below, the peaks of Sample 1 mainly relate to austenite with a cubic crystal lattice. Since the phase transition takes place below room temperature, the material is in austenitic phase. For Sample 2, whose A_p lies above room temperature, mainly martensite phase is expected. The spectrum, however, shows that both phases - martensite and austenite - are in coexistence. As seen from DSC investigations, the B19´→ B2 transformation in Sample 2 starts already at 26 °C. However, the temperature within our X-ray diffractometer lies above room temperature at ~ 34 °C. Reason for the austenite phase is therefore an already started phase transition.

To dynamically investigate the phase transformation, Sample 3 was investigated at changing temperature. Its temperature increased steadily from around -200 °C (LN_2) to around 34 °C while various spectra where recorded. The scanned 2θ range (47.5° - 52.5°) covers austenite and martensite peaks. The R-phase was found to be involved in the phase transition, as we find a peak associated with a rhomboedrical lattice appearing and vanishing during warming of the sample. This indicates a two step transformation via the R-phase (B19` → R-phase → B2) in our SLM specimens.





CONCLUSION & ACKNOWLEDGEMENT

By XRD, different crystallographic structures were identified in our SLM specimens, which have been produced with varied energy densities and subsequent solution annealing. Besides the austenite - martensite transition, we find a two step transformation route via the R-phase, which only exists in a narrow temperature range and does not appear in the DSC-curves. The SLM process allows the production and simultaneously tailoring properties of complex shaped NiTi specimens in only one fabrication step. Furthermore, anisotropic properties can be achieved. Based on these findings we will realize NiTi-scaffolds in which several effects can be exploited for an advanced performance.

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References: [1] ASTM International, F 2063-05. [2] Bormann T. et al. (2010), Proc. SPIE 7804: 78041. [3] Allafi J.K. (2002), Dissertation. [4] Otsuka K. et al. (2005), Prog Mat Sci 50: 511-678.