Ex-situ and in-situ TEM analysis of the nanocrystallization of bulk NiTi shape memory alloys made amorphous by repeated cold rolling

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NiTi alloys show a shape memory effect and superelasticity that can be used for various applications including sensors, actuators and medical devices. These functional properties are based on a martensitic phase transformation that strongly depends on the chemical composition. In addition, the martensitic phase transformation can be controlled by grain size [1]. In the present work, bulk nanostructured NiTi alloys were subjected to severe plastic deformation by repeated cold rolling (RCR). The RCR causes strong grain refinement and amorphization. High deformation degrees lead to an almost completely amorphous phase and upon annealing, nanocrystallization occurs [2]. The kinetics of the nanocrystallization can depend on both, the parameters of the annealing treatment and the degree of deformation, therefore allowing to control the final grain size. The aim of the present work is to analyze the kinetics of the nanocrystallization of RCR deformed NiTi using ex-situ and in-situ TEM experiments.

A NiTi alloy with a nominal composition of Ni-50.1 at.% Ti was produced by arc melting in cold crucibles using pure components (Ni, 5N and Ti, 4N) under an atmosphere of flowing argon. Plates were cut and subjected to RCR up to deformation degrees of ε ~ 17. The structure after severe deformation is almost completely amorphous. However, small crystalline debris survives the deformation and is heterogeneously distributed. Upon annealing up to 307°C nanocrystallization occurs. Ex-situ nanocrystallization was carried out in a calorimeter to precisely control the temperature. The total reaction time is about 270 min (determined by calorimetry) and was interrupted 10 times to prepare TEM samples to be analyzed at room temperature. A Libra 200 FE is used for ex-situ TEM analysis and a Hitachi H-800 is used for TEM in-situ heating experiments. For the in-situ experiments a Gatan 652-Ta double tilt heating holder was used.

Figure 1 shows the structure of ex-situ samples after 81 and 216 min. Grains in the amorphous phase grow spherical until they impinge upon each other. After 216 min of ex-situ heating only a very small amount of amorphous phase can be detected by electron diffraction and TEM bright- and dark-field images. The final number weighted mean grain size is about 80 nm, as determined by evaluating dark-field images taken from the ex-situ samples. The grain size distribution obtained by nanocrystallization is bimodal. In-situ heating at nominal 307°C shows that after impingement of the crystallites, no remarkable grain-growth occurs. Results of the in-situ heating experiment are shown in Figure 2. After 240 min still remarkable amorphous regions can be observed. In-situ heating up to 400°C shows small indication for grain-growth and heating up to 500°C shows clear indication for grain-growth.

The debris structure before nanocrystallization is determining the structure after nanocrystallization; since the pre-existing debris grows from the very beginning of the reaction, whereas newly nucleated grains start growing later a bimodal structure forms. Moreover, from the in-situ heating experiments it can be concluded that hard-impingement is present. Therefore, evaluation of the ex-situ grain sizes and grain size distributions after nanocrystallization can be used to analyze the crystallization kinetics. Similar to crystallization of equiatomic NiTi made amorphous by sputter deposition or melt spinning [3,4], the crystallization of RCR NiTi is polymorphic. Using the activation energy for crystallization as determined by the authors by calorimetry previously, the deviation of the temperature in-situ in the TEM foil from the nominal temperature can be estimated to be about 5°C.
References


Figure 1. Ex-situ TEM bright-field images of the nanocrystallization of RCR NiTi. The nanocrystallization at 307°C was interrupted after a) 81 min and after b) 216 min. Spherical particles grow in the amorphous phase and finally impinge with each other forming a bimodal grain size distribution.

Figure 2. In-situ TEM bright-field images during heating at nominal 307°C. The images were taken after a) 60 min, b) 120 min, c) 180 min and d) 240 min. Even after 240 min the sample is not fully crystalline. Grain-growth in the crystalline area is not detected whereas growth of grains in the amorphous phase occurs.