Shape memory alloys (SMA) show unique properties based on a martensitic phase transformation. The martensitic structures and interfaces control shape memory and superelasticity. Crystal size at the nanoscale can strongly impact martensitic phase transformations. The present work reports recent results of transmission electron microscopy (TEM) studies of phase transformations, defect structures, and martensitic interfaces of nanostructured SMA obtained by different processing routes.

Bulk nanocrystalline SMA alloys can be processed by methods of severe plastic deformation (SPD). As shown by TEM bright field (BF) and dark field (DF) images, SPD of ferromagnetic NiMnGa SMA yields strong grain refinement. Using TEM diffraction, concomitant disordering of the tetragonal martensite and a phase change to a face centred cubic structure is observed. Upon heating, the ordered Heusler austenite forms similar to that of the coarse grains. However upon cooling, TEM lattice fringe images and selected area diffraction shows that in the small grains a highly defective structure of modulated 14M martensite arises.

Highly localized processes of amorphization in NiTi-based and CuZr-based SMA subjected to SPD were analysed. Figure 1a shows SPD processed CuZr. While the density of dislocations is rather low, numerous deformation bands intersect the twinned martensite. Bands that extend several hundreds of nm while their width is several nm only frequently show intersections and bifurcations. HRTEM (cf. Figure 1b) and nanodiffraction reveal that bands contain an amorphous phase. Opposed to models predicting localized amorphization by accumulation of dislocations at twin boundaries, the bands are rather intersecting them. While SPD amorphization of NiTi is almost complete, TEM shows a high density of nanocrystalline debris. Upon heating, debris acting as nuclei strongly impacts crystallization kinetics. Figure 2 shows the results of TEM in-situ heating yielding a rather high nucleation rate while the rate of growth is very small causing nanocrystallization.

Strong size effects on martensitic phase transformations can arise by the high surface-to-volume ratio of freestanding nanocrystals. Figure 3a to c shows TEM images of core-shell nanospheres processed by femtosecond laser ablation of NiTi targets. A single laminate of twinned martensite is observed in smaller martensitic cores of the nanospheres (cf. Figure a and b) while larger cores can host self-accommodated groups of different martensitic laminates.

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Fig. 1: Nanoscale amorphization of CuZr. (a) TEM BF image of twinned Cm martensite containing numerous amorphous nanobands. Frequently bands mutually intersect (e.g. near A) and show branching (near B). (b) HRTEM image. A nanoband inclined to the (001) twin boundaries (dashed lines) runs parallel to (1-10) lattice planes (full lines). (BD=[110]).

Fig. 2: Nanocrystallization of NiTi. TEM in situ heating (temperature of 377°C). (a) BF images of nanocrystals embedded in the amorphous matrix. (b) After 51 min of heating new nanocrystals (marked by arrows) nucleated isolated from each other. (c) Diameter of four nanocrystals measured as a function of time showing constant rates of growth.

Fig. 3: TEM images of core-shell nanospheres processed by laser ablation of NiTi targets. The core contains NiTi with a martensitic B19' structure. (a) and (b) Nanoparticles with a core diameter of 45 and 75 nm, resp., containing a single laminate of twinned martensite. (c) Nanoparticle with a core of 83 nm diameter containing at least two laminates.