

Xenon Focused Ion Beam in the Shape Memory Alloys Investigation – The Case of NiTi and CoNiAl

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The presented article reviews the first experiences with the xenon plasma focused ion beam (FIB) in the scanning electron microscope (SEM) applied on the investigations of shape memory alloys (SMAs). The SMA are the focus of investigation in our department for many years and these investigated alloys are examples of material prepared by novel spark plasma sintering method (NiTi) and traditional metallurgical method (CoNiAl). Thus apart of basic characterization it also facilitates the comparison between two different methods of preparation.

The shape memory effect was described for the first time in AuCd alloy as a curiosity in 1932 by Ölander. The natural background of the effect – the reversible martensitic transformation was found in fifties, nevertheless until the discovery of the NiTi alloy in 1963 it remained a curious consequence of phase transformation with symmetry reduction. The great progress began after 1971 when the first application of SMAs appeared [1].

The Ni-Ti alloys remained the principal applied alloy mainly for the medical applications. The martensitic transformation proceeds mainly between B2 cubic phase, called austenite, and low-symmetric monoclinic B19' phase. Nevertheless, transformation process is complicated and other types of martensite can appear [2]. The preparation process is challenging due to the high titanium reactivity. In the present work the spark plasma sintering (SPS) process is used for the bulk material preparation from the elemental powders. The heating rate was scanned to optimize sintering process and the effect of powder graininess was studied as well. The desired state is fully compacted structure, as the material shall be used as the raw product for the wire drawing.

Quite opposite examples of SMA are CoNiAl based alloys prepared by classical metallurgy. We studied $\text{Co}_{38}\text{Ni}_{33}\text{Al}_{29}$ alloy. The high-temperature (austenitic) structure is again B2 and it transforms to tetragonal L1_0 martensite. In contrast to NiTi no other low-symmetry structures were observed but other phase particles are present even in the B2 matrix. Those are disordered A1 – FCC cobalt solid solution and its ordered version L12, which can be both presented in some particular ratio. From the previous studies is known that the transformation temperature is quite low around 200 K, but stress induced transformation can be induced up to room temperature. The stress induced martensite can be stabilized either by sample's geometry or by non-transforming A1 phase particles and thus easily observed (Fig.1). This stabilized martensite lamellae were wrongly considered as stable martensite as shown by in-situ neutron diffraction [3] and temperature dependence of magnetization [4]. Finally, the stress induced transformation can be induced by compression which results in pseudoelastic behavior at room temperature. The pseudoelastic behavior depends strongly on crystal orientation, which is consequence of orientation dependence of elastic constants and resulting large elastic anisotropy.

The full tensor of elastic constants and its temperature dependence was measured by resonant ultrasound spectroscopy (RUS). Although the CoNiAl is ferromagnetic SMA the effect of magnetoelastic coupling was found to be weak [5]. Nevertheless, the tendency of matrix toward the tetragonal distortion; i.e. stress induced martensitic transformation; can be attributed to atoms redistribution during annealing and quenching. The equilibrium state samples – Bridgman method grown crystals do not show the tendency toward stress induced transformation. The annealed and quenched non-equilibrium samples, which have high-temperature state with cobalt enhanced B2 matrix, relax performing nanoprecipitation or its precursors had such behavior.

The FIB technique using mainly highly intensive xenon beam is useful tool to investigate complicated morphologies in 3D, which are distributed on wide scale, while exhibiting only subtle differences of composition [6].

References:

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Figure 1. Lamellae of L₁₀ martensite stabilized at room temperature by A1 particles in B2 matrix of the annealed and quenched Co₃₈Ni₁₃₃Al₂₉ alloy. The example shows the structure investigated for stress induced lamellae interaction with A1 precipitates.