Experiment Report Form

	Experiment title: Ni-Mn-Sn-Co metamagnetic shape memory alloys thin films. Martensitic transformation and crystallographic stress studies by means of grazing surface X-ray diffraction	**Experiment number**: 25-02 885
Beamline:	**Date of experiment**: from: 26/10/2016 to: 29/10/2016	**Date of report**: 14/02/2017
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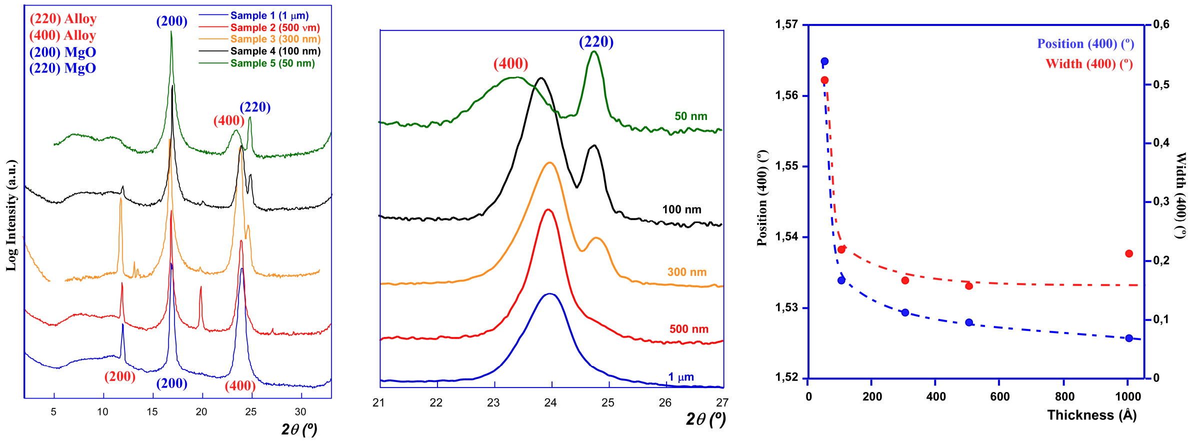
Report:

Metamagnetic shape memory alloys (MMSMAs) represent a promising kind of materials due to their ability to undergo large strains (>10%) under moderate external magnetic fields. Beyond their bulk applicability, their processing as thin films is especially interesting in view of the enhanced properties of the MMSMAs. The development of MMSMAs/substrate thin films composites involves crystallographic constraints imposed by the substrate that could either significantly impede or promote martensitic transformation depending on the type of substrate and thin film thickness. The enhancement of the spontaneous strains associated with the martensitic transformations is strongly related with the lattice misfit between film and substrate, and crystallographic defects both responsible for the induced strain in thin films. For this reason it is important to study both the crystallographic strains (conjugated with internal stress) generated in the austenitic and martensitic phases in MMSMAs thin films and their influence on thermally induced martensitic transformation and related functional properties.

With the aim to uncover the relation between the crystallographic stress imposed by the substrate on Ni-Mn-Sn-Co films properties, the study of the crystallographic stress vs. thin film thickness on six Ni-Mn-Sn-Co films attached to MgO (100) substrate has been carried out.

Sample 1: 1μm**, Sample 2:** 500 nm**, Sample 3:** 300 nm**, Sample 4:** 100 nm**, Sample 5:** 50 nm



(a) **(b)** **(c)**

Fig. 1 (a) Full scans of thin films. (b) Detailed 2θ (º) range of the (400) reflection. (c) (400) 2θ (º) position dependence with the thin film thickness.

As it is expected in the full diffraction patterns, the thin films show an (100) epitaxial growth of the Ni-Mn-Sn-Co alloy on MgO (100) substrate. Despite the MgO is suposed to be perfectly aligned on the (100) planes, the presence of (220) diffraction maxima is discovered in the substrate as the alloy thickness decreases. So the NiMnSnCo film on MgO substrate is not completely epitaxial. The films 1, 2 and 3 show clearly the (200) and (400) planes of the NiMnSnCo alloy, while in the films 5 and 6 (4 and 5?) there is a small contribution of the (220) reflection, while the (400) maxima is broadened considerably. There is also a progresive displacement of the (400) planes to lower 2θ(º) values, and hence, an increase of the cell parameter due to the Film-substrate misfit. The figure 1 (c) plots the evolution of the 2θ(º) position and medium half width of the (400) against the film thickness. Taking into account the position shift and the half-width of the (400) maxima, crystallographic strain effect due to the misfit between the substrate and the film are clearly observed only in films thinner than 300 nm.

Rocking curves

Starting from the maximum intensity 2θ(º) angle for the (400) reflection, a horizontally aligned sample was tilted in ψ(º) and χ(º) perpendicular angles, recording the intensity of the signal. The distribution of the intensity is the consequence of disaligned and/or strained single crystal domains/crystals in the thin film. As it is expected, the dispersion of the (400) planes in the ψ(º) and χ(º) angles is bigger in the thinner thin films, as a consequence of the strain imposed by the MgO substrate.

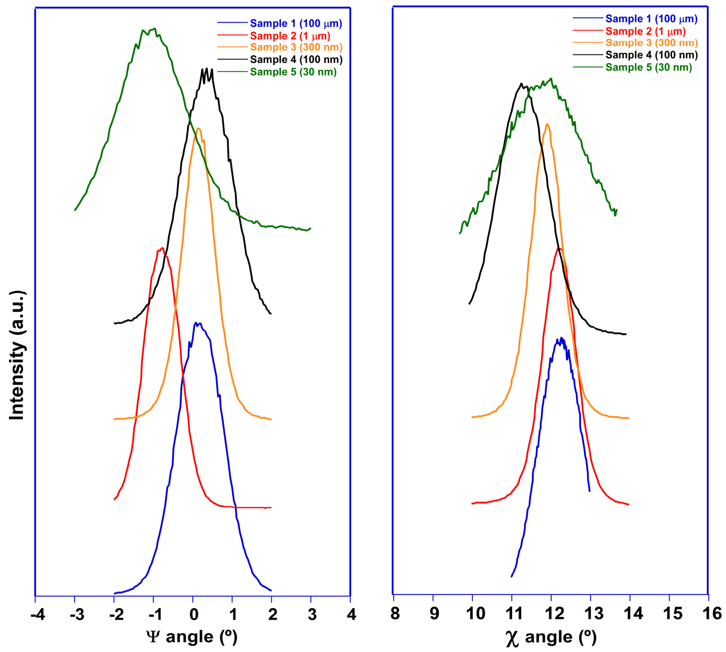


Fig. 2 . ψ(º) and χ(º) tilting angles rocking curves.

For each sample, the position, intensity and half width was determined for the interval of ψ(º) and χ(º) angles in which any signal is observed. The deviation of the d(400) spacing form the initial value for positive and negative tiltings of the χ(º) angle are observed in the figure 3. The differences from the +χ(º) and - χ(º) values in the displacement of the sample are indicative that the sample is disaligned with respect to one of the maximun stress axes of the deformation ellipsoid of the samples. For the ψ(º) the d(004) value is almost constant for the positive and negative tiltings, indicating that the samples are aligned in the same direction that one of the axis of the deformation ellipsoid.

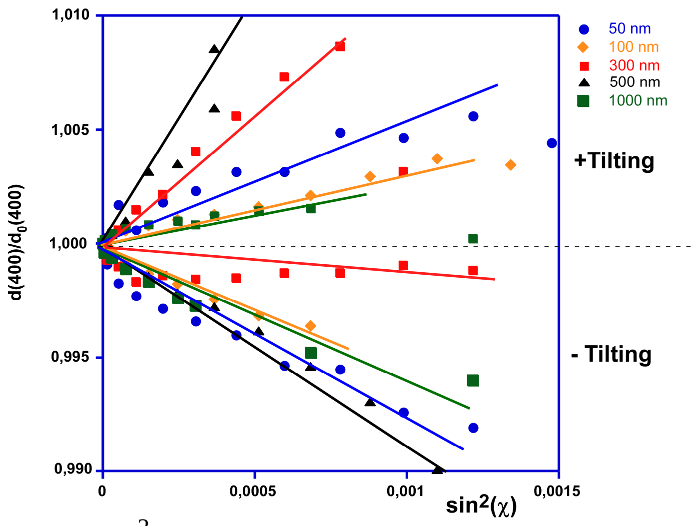
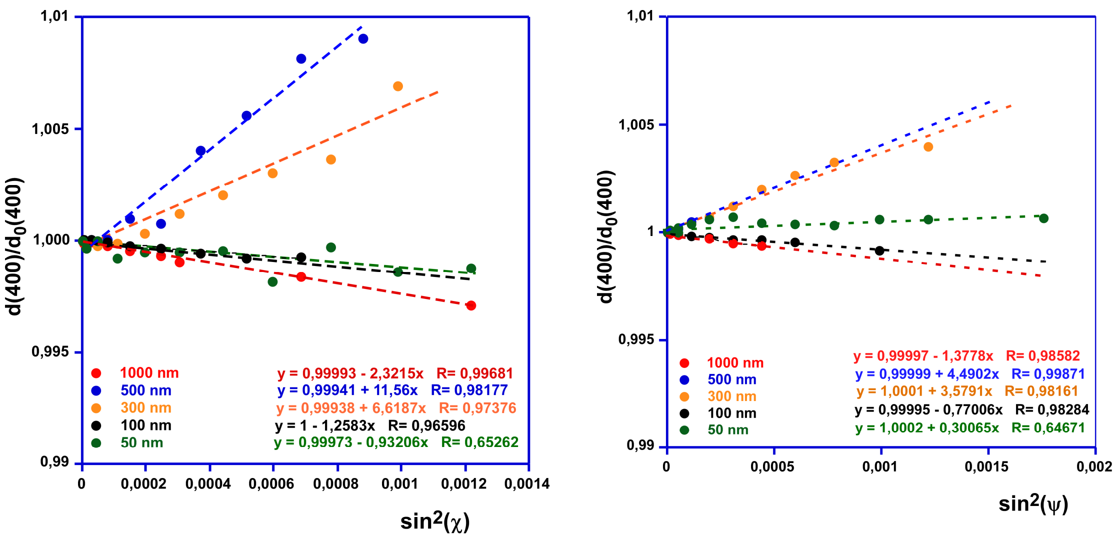


Fig. 2 . $\sin^2\chi$ vs. normalized d(400) spacing plot.

The average values of positive and negative tiltings for χ and ψ allow determining the average stress of the sample in the measured direction. If the data obtained from the χ and ψ scans are taken into account solely, the slopes of the plots indicate that the most stressed samples are the 500 nm and 300 nm thin films. However, the diffraction maxima of 500 nm and 300 nm films show extra (220) maxima of the Ni-Mn-Sn-Co alloy, so the sample is not completely epitaxially grown on the substrate. For the Films 1, 4 and 5, the slopes of the curves in the sin2 ψ(º) and χ(º) plots reveal similar stress values. The values have to be taken

carefully, because they are not the maximum stress values of the films, at least for the χ(°) tilting experiments, in which the lateral stress is evident, as is observed in the figure 2

The sin2 plots reveal a non homogeneous distribution of the stress in the thin film surface. The values obtained from the sin2 χ(°) plots are far from the maximum stress vector of the deformation ellipsoid. More measurements are needed, at least one in between the mesurement direction of χ and ψ angles to determine the real oriention of the deformation vectors within the surface of the thin films.



(a) **(b)**

Fig. 3 . (a) $\sin^2\chi$ and (b) vs. $\sin^2\psi$ average vs. normalized d(400) spacing plot.

It would be very helpful to carry out also measurements in thinner samples. There is need to explore the reciprocal space of the thin film samples to assure that there is a good epitaxial growth of the film, and after that, to determine experimentally which is the crystallographic relation between the MgO substrate and the thin film.