Ni-Mn based ferromegnetic shape memory alloys: formation and characterization

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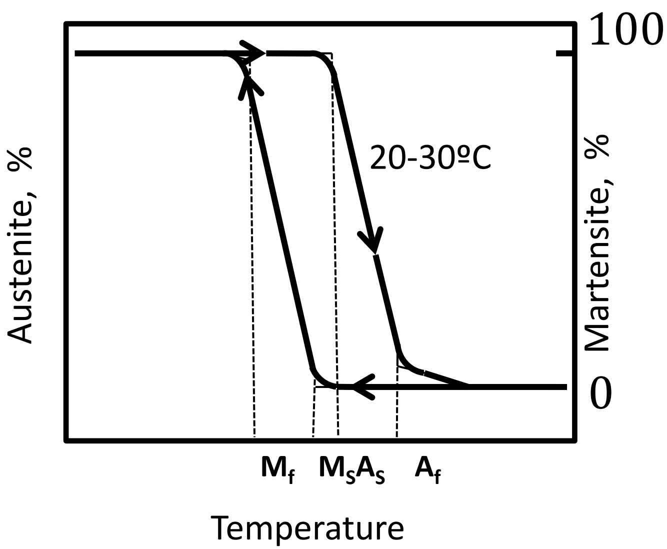
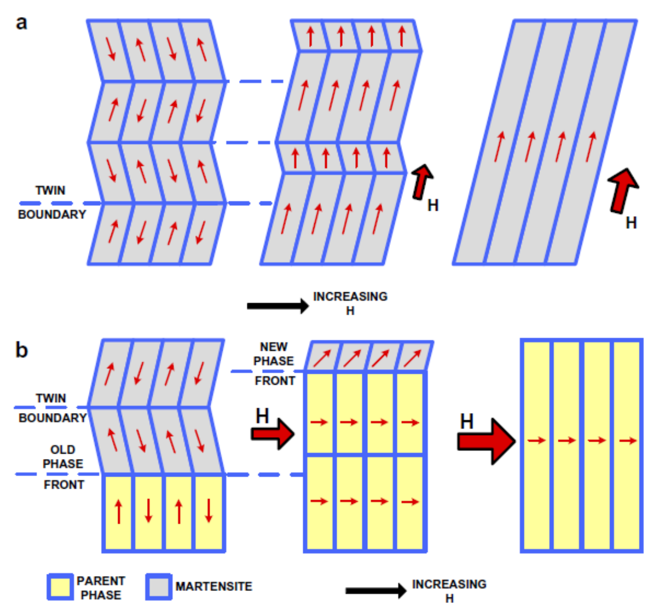
Supervisor: AP Wojciech Maziarz

Project is co-financed by European Union within European Social Fund

Introduction



Schematics of reversible martensitic phase transformation upon cycling.



Effect of applied magnetic field H on the reorientation of the martsnite twin variants (a), and phase transformation (b) in MSMAs.

Ref: H. E. Karaca, I. Karaman, B. Basaran et al. *Acta Materialia* 55 (2007) 4253-4269.

MOTIVATION

Most extensively studied NiMnGa (high cost, low Ms)

Bulk polycrystalline

$Ni_{50}Mn_{50}Sn_x$ (10<x<16.5) Y. Sutou et al. Appl. Phys. Lett. 85 (2004)
$Ni_{50}Mn_{50-x}Sn_x$ (5<x<25) T. Krenke et al. Nat. Mater. 4 (2005)
$Ni_{50}Mn_{36}Sn_{14}$ P. J. Brown et al. J. Phys.: Condens. Matter 18 (2006)
$Ni_{50+x}Mn_{37-x}Sn_{13}$, $Ni_{50+y}Mn_{39-y}Sn_{11}$ (x, y = 1, 2, 3) V. Khovaylo et al. Adv. Funct. Mater. 13 (2006)
$Ni_{50-x}Mn_{39+x}Sn_{11}$ (x=5,6,7) Z. D. Han Appl. Phys. Lett. 90 (2007).

Ribbons

$Ni_{50}Mn_{37}Sn_{13}$ J. D. Santos et al. J. Appl. Phys. 103 (2008)
$Ni_{50.3}Mn_{35.3}Sn_{14.4}$ B. Hernando et al. Appl. Phys. Lett. 92 (2008)
$Ni_{50}Mn_{37}Sn_{13}$ B. Hernando et al. J. Magn. Magn. Mater (2009)
grain oriented
Advantages :
-avoiding the homogenization step to reach a single phase alloy,
- synthesis of highly textured polycrystalline samples

e/a tuned by substitution or compostitional variation
eg. Cr, Fe, Co, Cu

Conventional

$Ni_{43}Mn_{46}Sn_{11-x}Al_x$ (x=0, 0.5, 1, 2) J. Chen, Z. Han, B. Qian et al. J. Magn. Magn. Mater 323 (2011)

Ribbons

NiMnSnAl **?**

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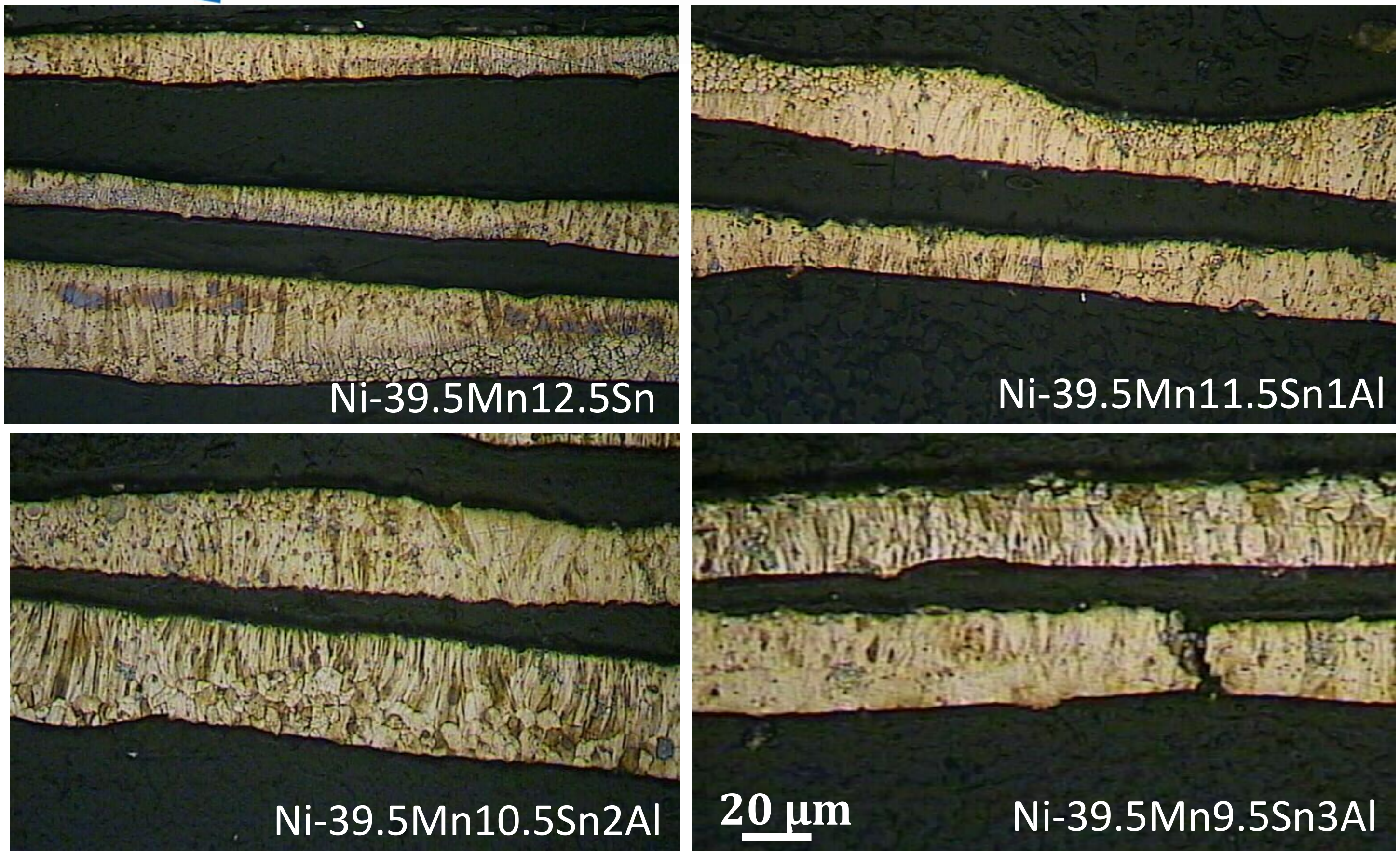
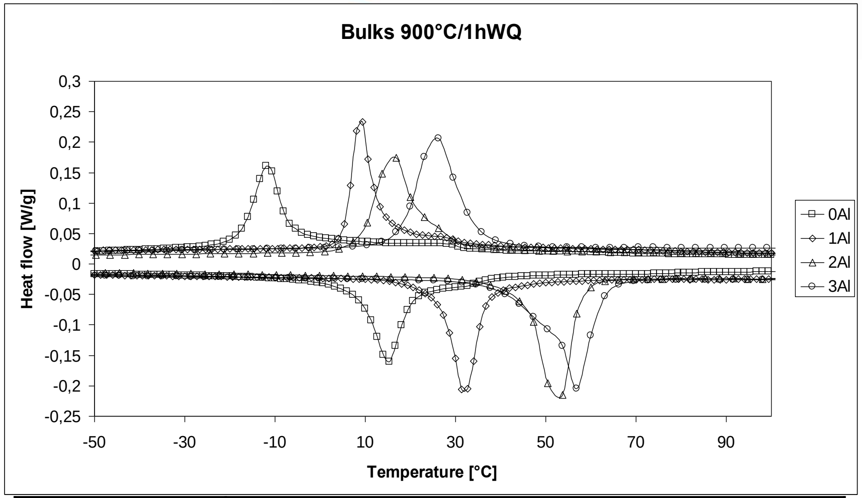
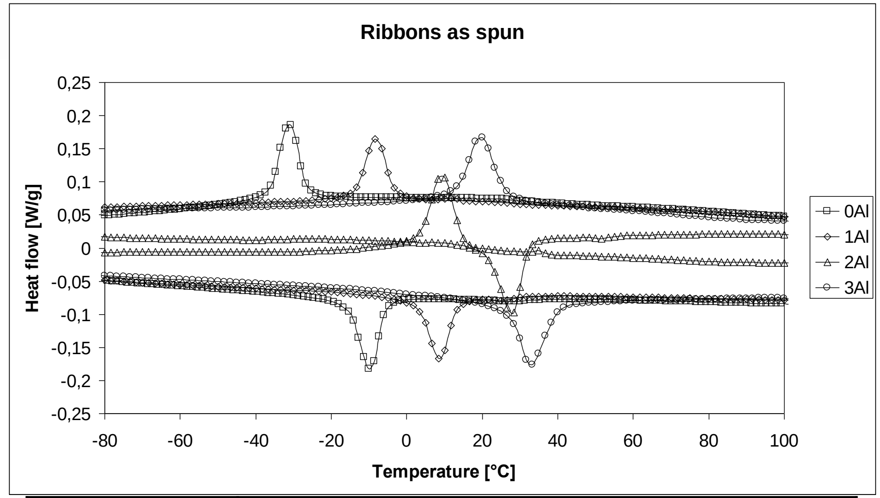


Optical microscopy images showing cross sections of ribbons. Visible non uniform microstructure composed of columnar grains growing perpendicular to the ribbon plane and smaller grains on the ribbon side in contact with the wheel. Such microstructure results from heat transfer kinetics occuring on rapid quenching.





Bulks	Transformation temperatures [°C]		
	T_{pA-M}	T_{pM-A}	ΔT
0Al	-12	15	27
1Al	9	31	22
2Al	17	54	37
3Al	26	57	31

Ribbons	Transformation temperatures [°C]		
	T_{pA-M}	T_{pM-A}	ΔT
0Al	-31	-10	21
1Al	-8	8	16
2Al	8	28	20
3Al	18	33	15

Figures illustrate DSC measurements of bulk and ribbon alloys. It is visible that the martensite start transformation temperature M_s increases with increasing Al concentration in both bulks and ribbon alloys. It is also observed that the M_s is higher for bulks as compared to ribbons what is related to grain size refinement during ribbons production.

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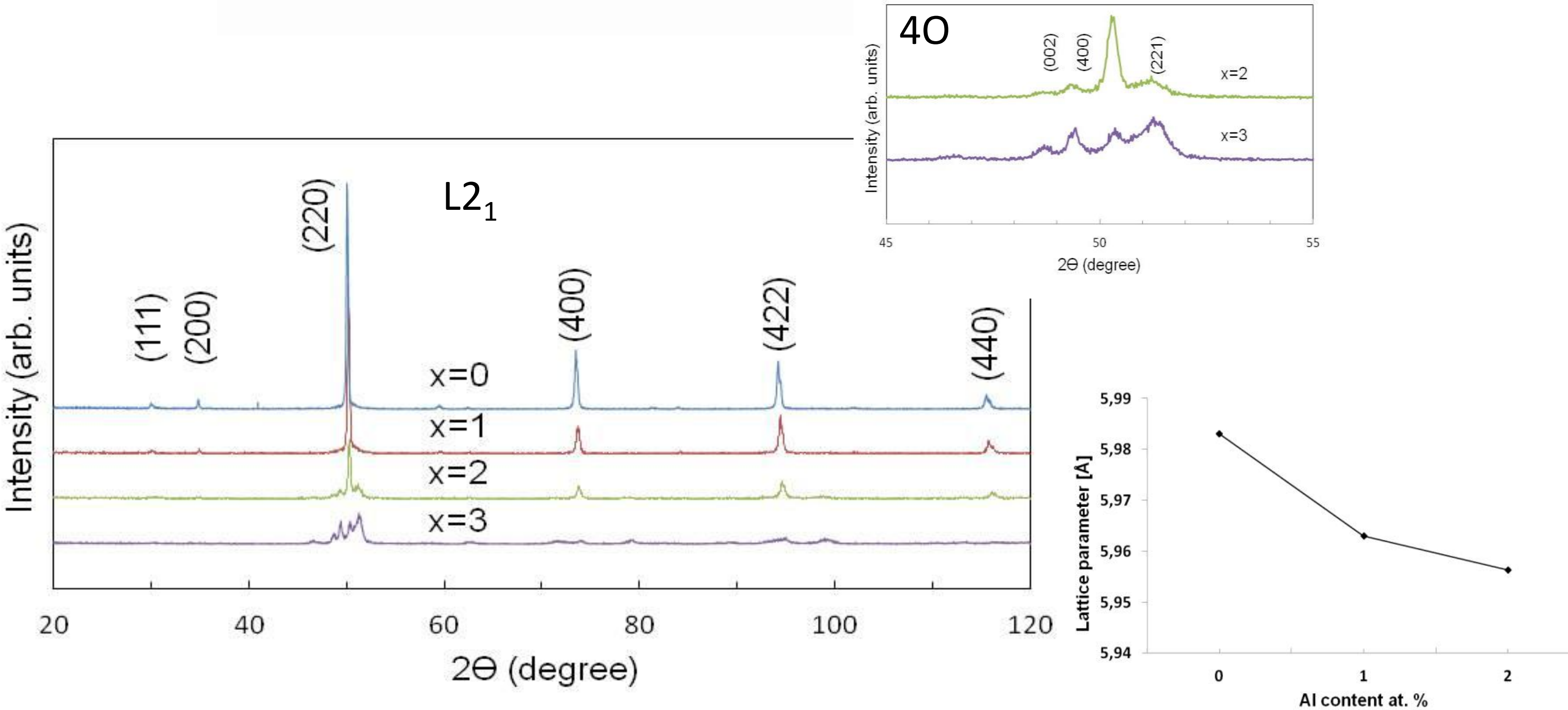
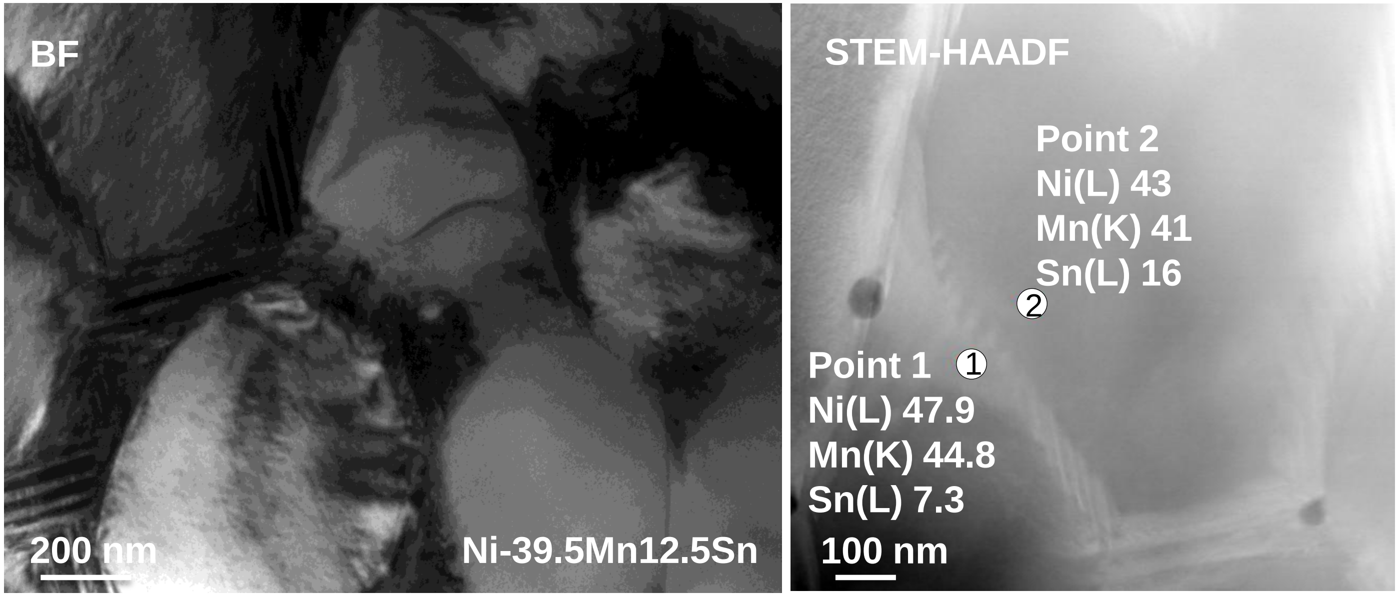
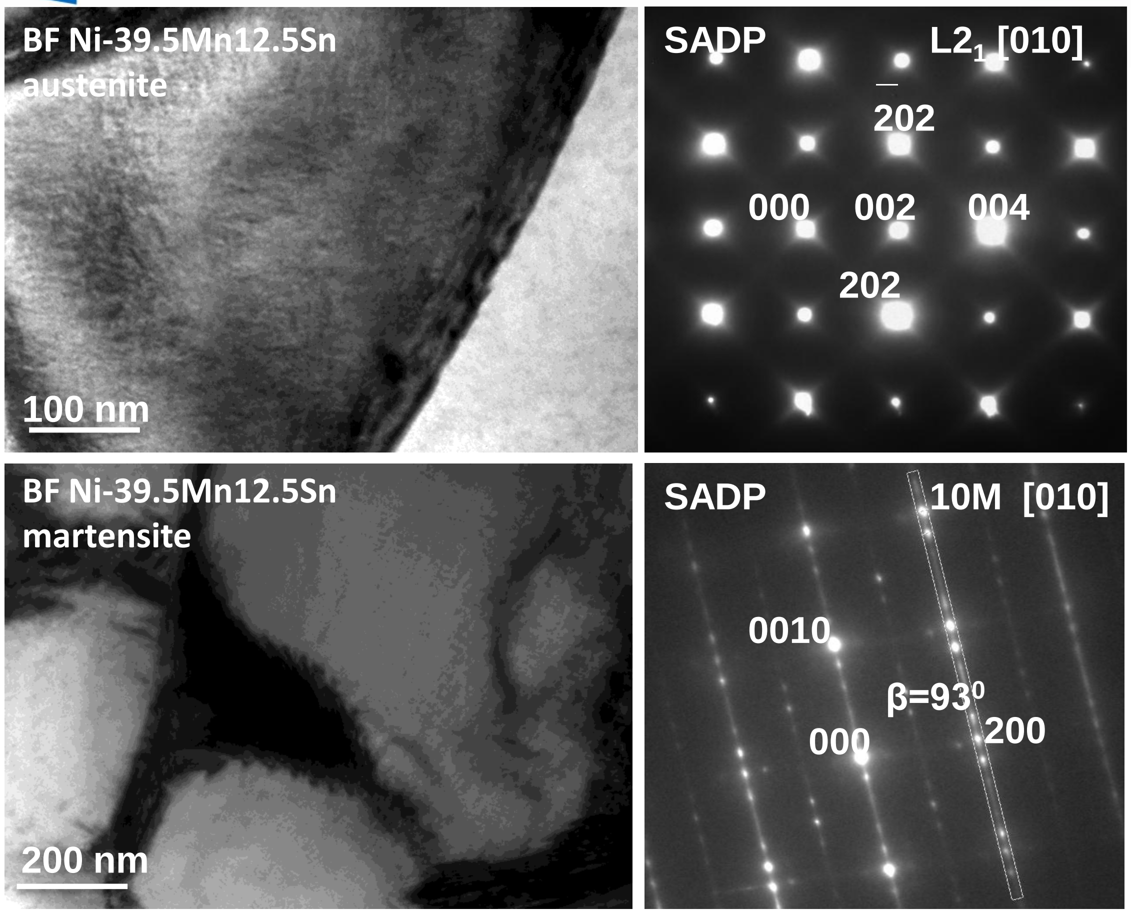


XRD patterns of ribbon alloys with varying amount of Al (0, 1, 2, 3 at.%). Profiles of ribbons containing 0 and 1 at. % Al correspond to $L2_1$ Heusler structure whereas profiles of ribbons with 2 at. % of Al contain austenite $L2_1$ and 4O martensite phases. Peaks corresponding to 4O martensite become even more pronaunced in alloy ribbon with 3 at. % Al. Also the lattice parameter vs Al content plot shows that the lattice constant decreses with increasing Al content what is attributed to the smaller atomic radius of Al as compared to Sn which it substitutes.



Bright Field and STEM-HAADF images of Al free alloy ribbon. Visible cellular and intercellular areas appearing darker on BF image. STEM-HAADF image confirms this dual microstructure. Chemical analysis at point 1 and 2 reveals compositional differences between these two areas. Intercellular area contains less Sn what then indicates the increase in valence electron concentration e/a. It is known that with increasing e/a martensite start transformation temperature increases. This therefore suggests that the darker phase corresponds to martensite whereas the brighter phase in the BF image corresponds to austenite.



Bright field (BF) images and corresponding selected area diffraction patterns (SADP) taken at room temperature from Al free alloy ribbon. The SADP corresponing to the brighter phase in the BF image can be indexed according to $L2_1$ structure and the darker phase is attributed to the 10 M martensite structure with monoclinic unit cell.

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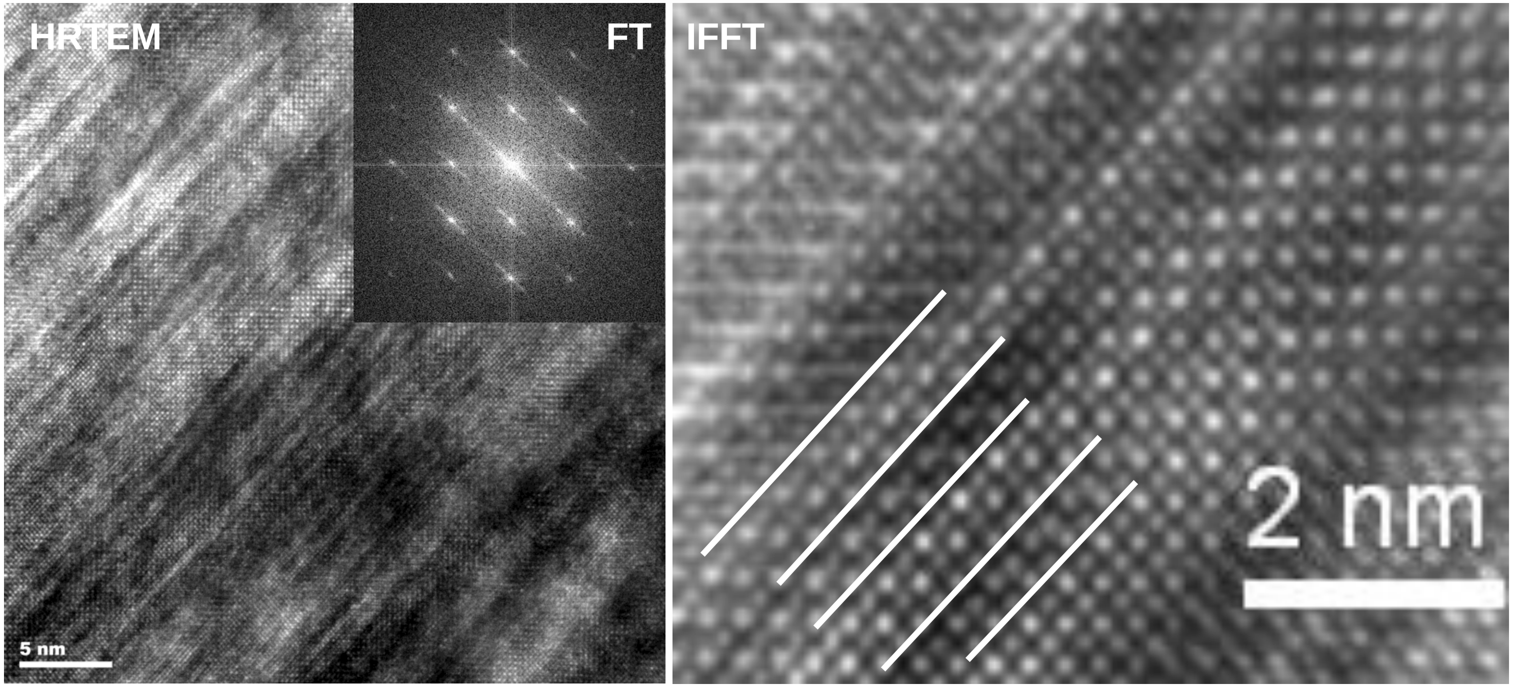
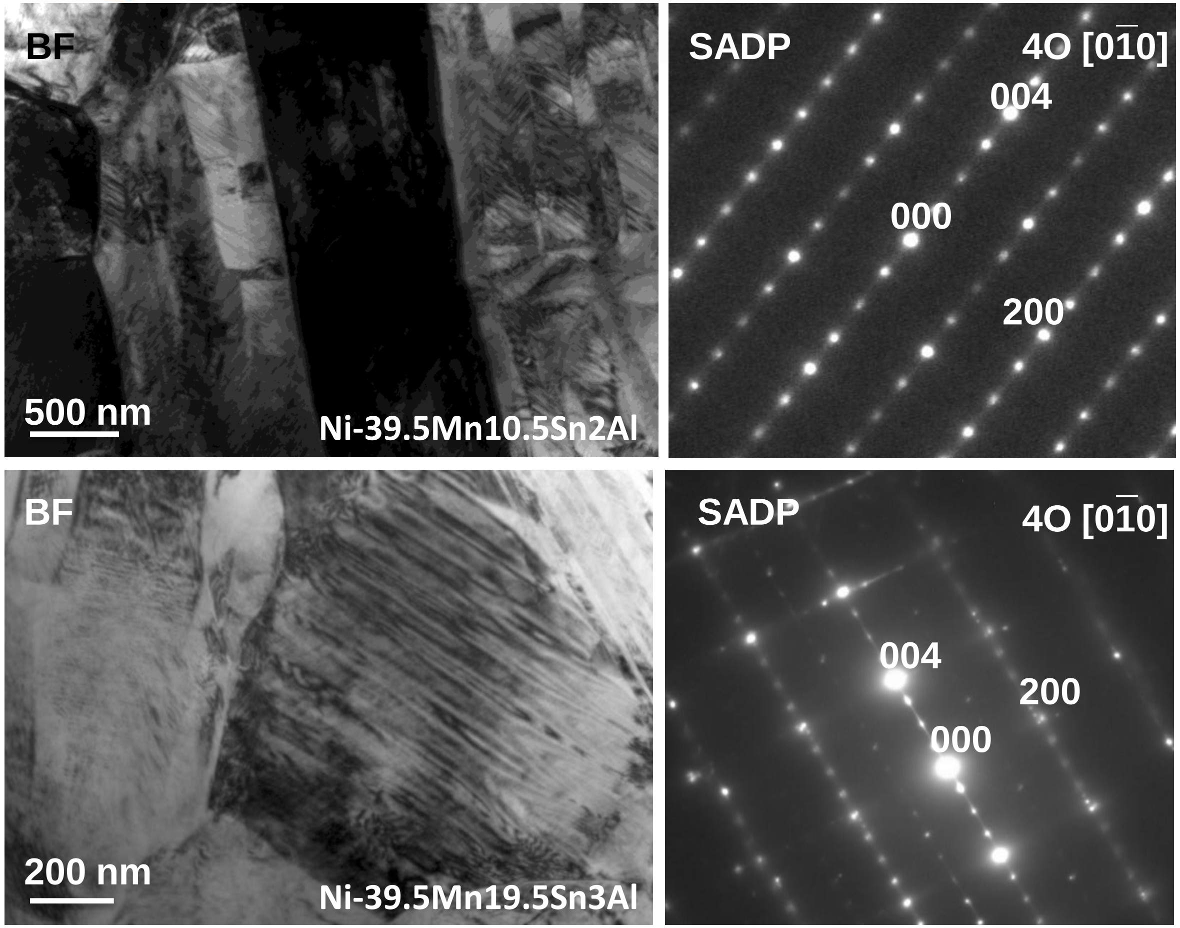


High Resolution Transmission Electron Microscopy (HRTEM) image, its corresponding Fourier Transform (FFT) (inset) and Inversed Fourier Transform (IFFT) obtained from 10 M martensite in Al free ribbon. Based on the IFFT image the peridoic stacking of planes can be determined as $(3\ \bar{2})$ according to Zhdanov notation.



Bright field (BF) images and their corresponding selected area diffraction patterns (SADP) taken at room temperature from alloy ribbons containing 2 and 3 at. % Al. More homogenous microstructure is observed on BF images as compared to BFs obtained for Al free ribbons. Both SADPs are attributed to 4O martensite.

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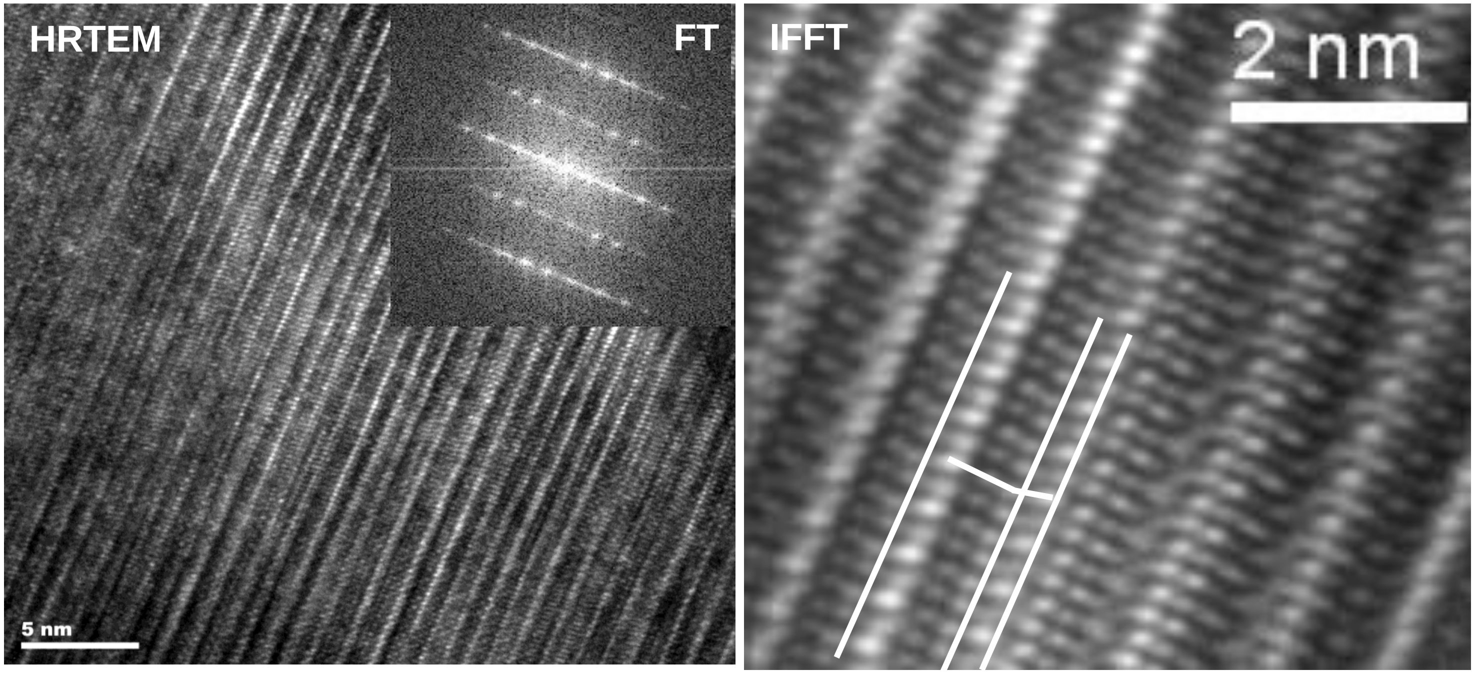

High Resolution Transmission Electron Microscopy (HRTEM) image, its corresponding Fourier Transform (FFT) (inset) and Inversed Fourier Transform (IFFT) obtained from 4O martensite in Al containing (2 at. %) ribbon. Based on the IFFT image the peridoic stacking of planes can be determined as $(3\ \bar{1})$ according to Zhdanov notation.

Interdisciplinary PhD Studies in Materials Engineering with English as the language of instruction
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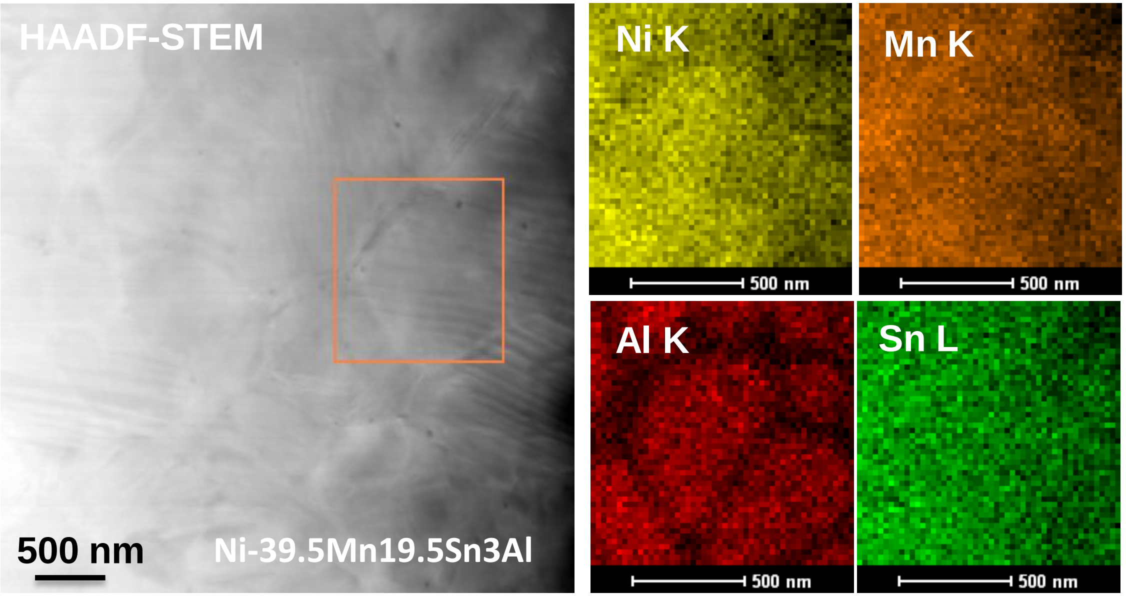

High Angle Annular Dark Field Scanning Transmission Electron Micrroscopy image of alloy ribbon containing 3 at. % Al and an elemental map taken from the area marked in red square on the HAADF-STEM image.
The map shows uniform distribution of Ni, Mn, Sn elements. Some nonuniforimty of distribution is observed with respect to Sn. This is related to the fact that Sn is the lowest melting point element in this system and it may be prone to segragation during crystallization.

Summary:

✓ A series of alloys with composition $Ni_{48}Mn_{39.5}Sn_{12.5-x}Al_x$ (x=0, 1, 2 , 3 at. %) has been obtained in a bulk form and in a form of ribbons using melt spinning technique,

✓ Obtained samples has been characterized using: optical microscopy (OM) - microstructure, X- ray diffraction (XRD) – phase identification, transmission electron microscopy (TEM) – structural studies, scanning transmission electron microscopy (STEM) – microstructure (average grain size), energy dispersive spectroscopy (EDS) – chemical composition, differential scanning calorimetry (DSC) – phase transition temperature and enthalpy of formation determination.

✓ The results have been presented at an international conference on a poster, an abstract has been published and a regular paper is underway.

Future work:

-VSM,

-Powder metallurgy

    -Partciles size (milling).

- Different compositions (Ni-Mn-In, Co, Fe, Al, Cu subsitutions).

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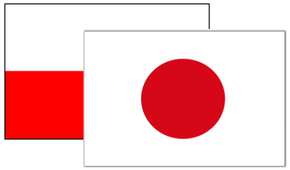
Publications and conferences

„The Effect of Al. Substitution on Microstructure and Martensitic Transition Of $Ni_{48}Mn_{39.5}Sn_{12.5-x}Al_x$ Heusler Alloy Ribbons” P. Czaja, W. Maziarz, J. Dutkiewicz, T. Czeppe - conference abstract + poster

„Microstructure and martensitic transformation in Al substituted NiMnSn Alloy ribbons” W. Maziarz, P. Czaja, M. Faryna, T. Czeppe, A. Góral, J. Dutkiewicz - conference abstract + poster + paper

The XXII Conference on Applied Crystallography
September 02-06, 2012, Targanice, Poland



„Structure and martensitic transformation in $Ni_{44}Mn_{43.5}Sn_{12.5-x}Al_x$ Heusler alloys” W. Maziarz, P. Czaja, T. Czeppe, A. Góral, J. Dutkiewicz - conference abstract + poster + paper

9th Polish-Japanese Joint Seminar on Micro and Nanoanalysis
10-13 September 2012, Sieniawa Poland

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