Structural, electronic and magnetic properties of the $Mn_{54-x}Al_{46}Ti_x$ (x = 2; 4) alloys

R. Gavrea[1], R.Hirian[1], S. Mican[1], D. Benea[1], O. Isnard[2], M. Coldea[1] and V. Pop[1]

[1] *Babeş-Bolyai University, Faculty of Physics, Cluj-Napoca, RO-400084, Romania*

[2] *Institut Néel, CNRS, Université Grenoble Alpes, BP 166X, 38042 Grenoble, Cédex 9, France*

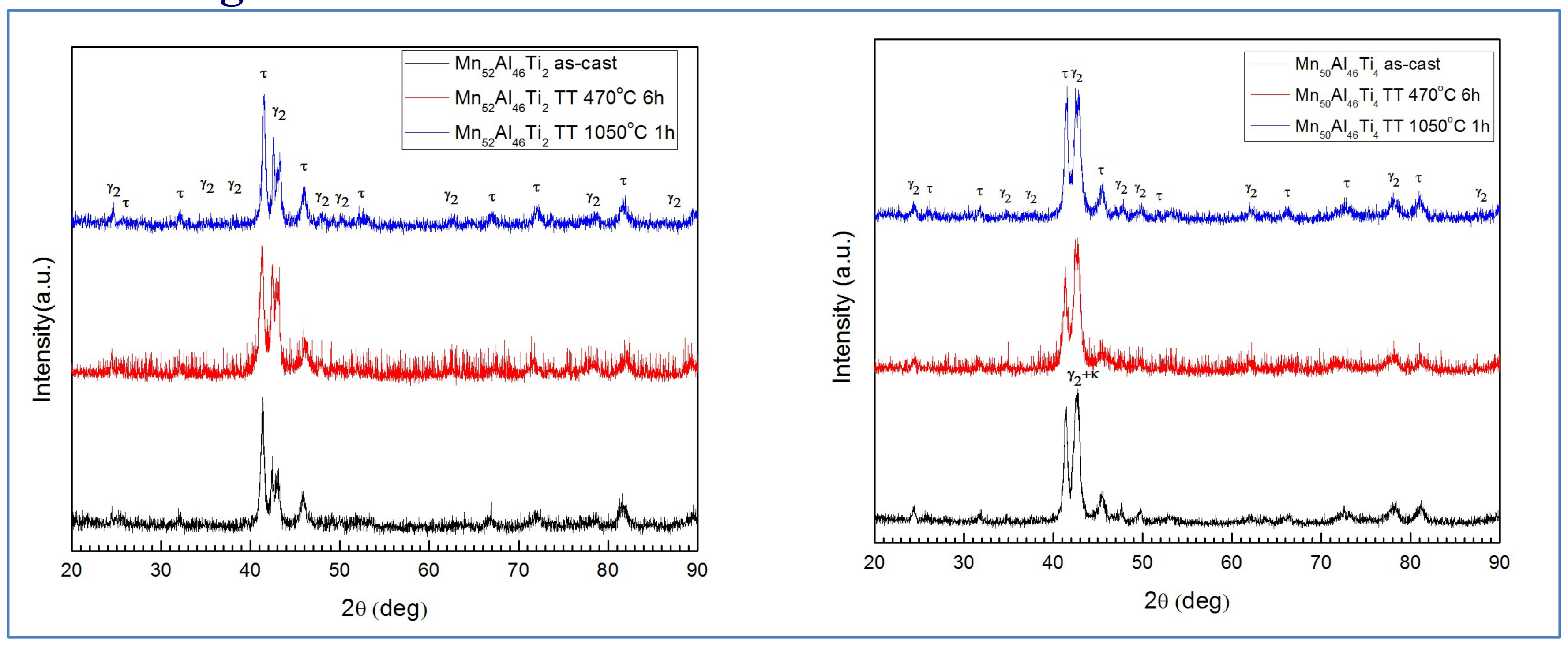
Abstract: The structural, electronic and magnetic behavior of the $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys have been studied through X-ray diffraction, electronic band structure calculations and magnetic measurements in the temperature range 4–850 K and magnetic field up to 7 T. Band structure calculations show a preference for Ti atoms to occupy the Mn sites in the plane of Al atoms with their magnetic moments (-0.66 μ_B/Ti) coupled antiparallel relative to the Mn magnetic moments in the plane of Mn atoms (2.33 μ_B/Mn). The as-cast and annealed samples were phase mixtures with different values of the hard ferromagnetic τ phase content. The ferromagnetic τ phase was found along with the nonmagnetic γ_2 phase in the as-cast $Mn_{52}Al_{46}Ti_2$ alloy. Except the as-cast and annealed at 1050 ºC for 1h $Mn_{52}Al_{46}Ti_2$ alloys, all the analyzed samples pointed out the presence of a soft γ-Mn phase with a Mn magnetic moment close to that found in the τ phase and with T_c around 500 K. The best magnetic characteristics were obtained for $Mn_{52}Al_{46}Ti_2$ alloy annealed at 470 °C for 6h: M_s=116 Am²/Kg at 4 K and T_c=660 K, in good agreement with the values reported in the literature for the τ phase of the MnAl system. The increase of the Ti content from x = 2 to x = 4 in $Mn_{54-x}Al_{46}Ti_x$ leads to the decrease of the τ phase content and consequently to the increase of the soft ferromagnetic γ-Mn phase. The electronic, structural and magnetic properties of these alloys are analyzed as a function of composition and preparation route and discussed in comparison with the properties of the $Mn_{54}Al_{46}$ parent alloy.

Experimental Details:

- The $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere and annealed at 470 ºC for 6h and 1050 ºC for 1h.
- High purity Mn (99.95 wt%), Al (99.999 wt%) and Ti (99.99 wt%) were used as starting materials.
- XRD investigations were performed using a Brüker D8 Advance X-ray diffractometer with Cu K_α radiation.
- Magnetization measurements were performed using an extraction magnetometer in the temperature range 4-800 K in applied external fields up to ±7 T.
- Electronic structure calculations were performed in the framework of the Local Density Approximation (LDA) of the Density Functional Theory using the SPRKKR method.

Results and Discussions :

XRD Investigations:



τ -phase → tetragonal $L1_0$ type structure, ferromagnetic

γ_2 -phase → Al_8Mn_5 type structure, non-magnetic

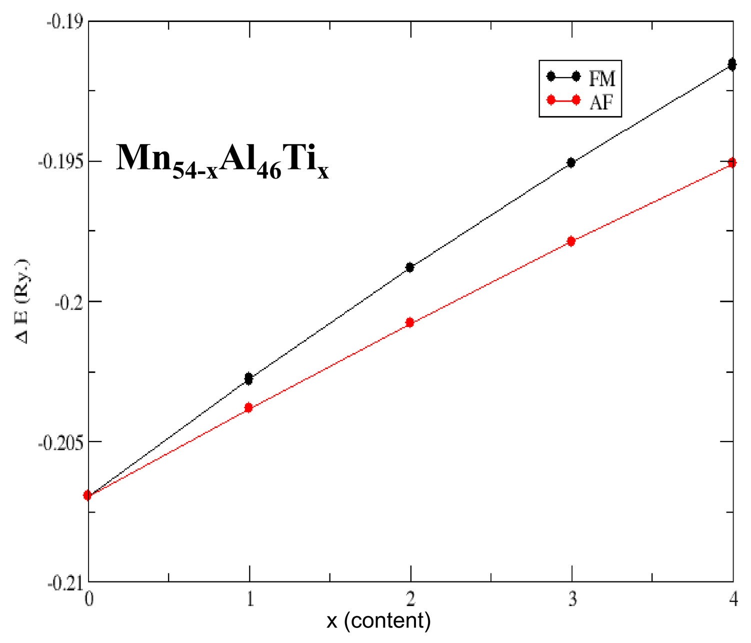
κ-phase → CsCl type structure, ferromagnetic

The concentrations values of the τ, γ_2 and k phases and the lattice parameters of the as-cast and annealed $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys.

Sample	c_τ (wt%)	$c_{\gamma2}$ (wt%)	c_κ (wt%)	Phase τ		Phase γ_2		Phase k
				a (Å)	c(Å)	a(Å)	c(Å)	a(Å)
$Mn_{52}Al_{46}Ti_2$ as-cast	75	25	-	3.96	3.50	12.58	7.90	-
$Mn_{52}Al_{46}Ti_2$ + 470C 6h	62	38	-	3.94	3.56	12.61	7.91	2.99
$Mn_{52}Al_{46}Ti_2$ + 1050C 1h	67	33	-	3.96	3.50	12.56	7.90	-
$Mn_{50}Al_{46}Ti_4$ as-cast	35	26	39	3.99	3.45	12.68	7.88	2.95
$Mn_{50}Al_{46}Ti_4$ + 470C 6h	52	29	19	3.99	3.46	12.66	7.85	3.01
$Mn_{50}Al_{46}Ti_4$ + 1050C 1h	43	30	27	4.00	3.43	12.68	7.80	2.99

- Volumes of the elementary cells of the $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys are approximately equals, suggesting a dilution limit for the Ti content in τ phase of these alloys of about 2%.
- The τ phase content decreases by increasingTi doping.
- The presence of the k -phase in $Mn_{50}Al_{46}Ti_4$ alloys.

Band Structure Calculations:

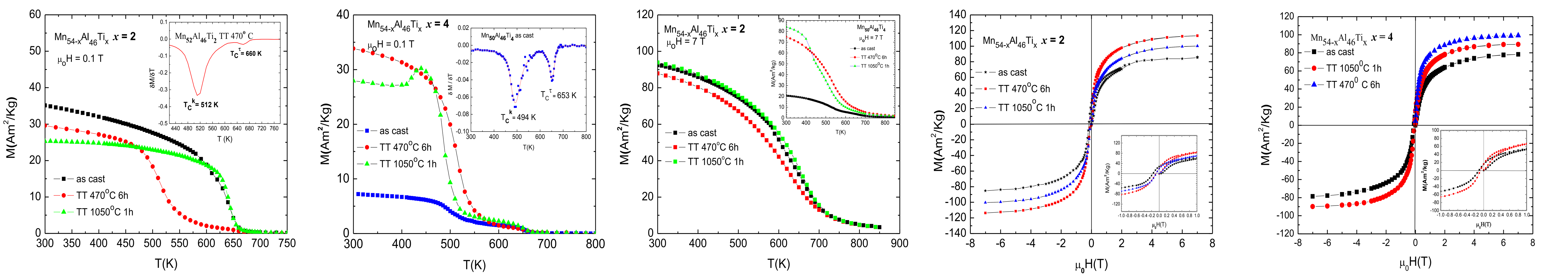


- A non-primitive face centered unit cell, space group P4/mmm (123) has been considered.
- The Mn magnetic moments in the Mn plane (Mn^{1a} and Mn^{1c} sites) are coupled antiparallel with the Mn magnetic moments in the Al plane (Mn^{2e} site).
- The smallest total energy of $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys was obtained for Ti atoms sitting on the *2e* sites.

Calculated magnetic moments for $Mn_{54}Al_{46}$ $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys in the AFM configuration.

		$Mn_{54}Al_{46}$ (a=3.93 Å c=3.57 Å)		$Mn_{50}^{1a,1c}(Al_{46}Ti_2Mn_2)^{2e}$ (a=3.96 Å c=3.50 Å)		$Mn_{50}^{1a,1c}(Al_{46}Ti_4)^{2e}$ (a=3.99 Å c=3.45 Å)	
		m_{spin} (μ_B)	m_{orbit} (μ_B)	m_{spin} (μ_B)	m_{orbit} (μ_B)	m_{spin} (μ_B)	m_{orbit} (μ_B)
2e	Al	-0.08	0	-0.08	0.00	-0.08	0.00
	Mn	-3.22	-0.01	-3.20	-0.01	-	-
	Ti	-	-	-0.68	0.00	-0.68	0.00
1a,1c	Mn	2.33	0.04	2.28	0.04	2.25	0.04
Total (μ_B/f.u.)		1.00	0.02	1.02	0.02	1.06	0.02

Magnetic Investigations:



M_s, T_c, H_c and M_r of $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys.

Sample	M_S (4K) (Am²/Kg)	M_S(300K) (Am²/Kg)	T_C^τ (K)	T_C^k(K)	H_C^{4K} (kOe)	H_C^{300K} (kOe)	M_r^{4K} (Am²/Kg)	M_r^{300K} (Am²/Kg)
$Mn_{52}Al_{46}Ti_2$ as-cast	91.20	93.50	642	-	1.64	0.88	27.48	21.05
$Mn_{52}Al_{46}Ti_2$ TT 470˚C 6h1	115.18	87.60	660	512	0.82	0.69	19.51	14.60
$Mn_{52}Al_{46}Ti_2$ TT 1050˚C 1h	102.31	98.54	643	-	0.77	0.54	19.51	17.45
$Mn_{50}Al_{46}Ti_4$ as-cast	80.50	81.21	653	494	1.13	0.43	15.84	11.02
$Mn_{50}Al_{46}Ti_4$ TT 470˚C 6h	99.2	75.54	657	515	-	0.34	-	11.02
$Mn_{50}Al_{46}Ti_4$ TT 1050˚C 1h	90.70	83.10	653	487	0.76	0.34	16.16	8.52

- The $Mn_{52}Al_{46}Ti_2$ annealed at 470 ºC for 6h sample pointed out the presence of the soft k-phase, although this phase was not observed in XRD investigations, probably due to the superposition with γ_2 phase.
- The soft k-phase is present in all $Mn_{50}Al_{46}Ti_4$ alloys.
- The second transition may be attributed to the ferromagnetic-paramagnetic transition of the hard magnetic τ phase of the Ti-doped samples.
- The increase of the Curie temperature for the τ-phases of these samples may be explained by the decrease of the antiferromagnetic interaction in comparison with the existing one in the parent alloy $Mn_{54}Al_{46}$.
- The coercive fields and the remanent magnetizations are diminished due to the presence of the soft k-phase component in the majority of the investigated samples.

Conclusions:

- All the analyzed samples contain **τ and γ_2 phases**, but the $Mn_{50}Al_{46}Ti_4$ alloys contain along these two phases also the **κ-phase** (CsCl-structure type).
- Band structure calculations show a **preference for Ti atoms** to occupy the Mn sites in the plane of Al atoms.
- The increase of the Ti content from x = 2 to x = 4 in $Mn_{54-x}Al_{46}Ti_x$ leads to the decrease of the τ phase content and consequently to the increase of the soft ferromagnetic κ-phase.
- The values of the Curie temperatures T_C^τ and T_C^k of the as-cast and annealed $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys suggest that **the solubility limit of Ti** in $Mn_{54-x}Al_{46}Ti_x$ is about 2%, in good agreement with the XRD results.

[1] R. Skomski et al., *Permanent Magnetism*. Institute of Physics, Bristol,1999.
[2] Y. Sakka, et al., *Journal of Materials Science*, vol. 24, 4331-4338, 1989.
[5] Hong Jian et al., Journal of Alloys and Compounds, vol. 622, 2015.
[3] J. Coey, *Magnetics, IEEE Transactions on*, vol. 47, 4671-4681,2011.
[4] H. X. Wang et al., *Open Journal of Microphysics*, vol. 1, 19-22, 2011.

Acknowledgment

This work was supported by the Romanian Ministry of Education and Research, Grant No. PN-II-ID-PCE-2012-4-0470 and PN-II-RU-TE-2014-4-2360.