Electronic and Magnetic Properties of $Mn_{50}Al_{46}M_4$ (M = Mn, Ni, Ti) Alloys

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Abstract: In this study we present the results of electronic structure calculations and the experimental investigations on the structural and magnetic properties of the $Mn_{50}Al_{46}M_4$ (M = Mn, Ni, Ti) alloys. The highest magnetic moment was found for the $Mn_{50}Al_{46}Ni_4$ alloy. Total energy calculations point to a more stable antiferromagnetic configuration of the Mn^{1a}-Mn^{2e} pair. DTA measurements pointed out the formation of the metastable τ phase around 470 ºC and its decomposition into the stable γ_2 and β-Mn(Al) phases at 850 ºC. The τ phase was found along with the ε' phase only in the as-cast sample and the ones annealed at 470° C. A maximum τ phase concentration of 50% was found for the sample annealed at 470 ºC for 6 h. The close values of the theoretical and experimental effective magnetic moments confirm the existence of the ε′ and τ phases in these alloys.

Experimental and Computational Details:

- Electronic structure calculations were performed in the framework of the Local Density Approximation (LDA) of the Density Functional Theory by means of the SPR-KKR method using the experimentally determined lattice parameters for $Mn_{54}Al_{46}$ (a = 3.94 Å, c = 3.58 Å). All relativistic effects have been taken into account, including the spin-orbit coupling, in the ferromagnetic (FM) and antiferromagnetic (AFM) spin configurations of the Mn^{1a}-Mn^{2e} pair.
- The $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere.
- The samples were annealed in an inert Ar atmosphere at temperatures between 470 and 850 ºC for different times followed by quenching in water.
- XRD investigations were performed using a Brüker D8 Advance X-ray diffractometer with Cu K_α radiation.
- Differential thermal analysis (DTA) was performed between 100 and 900 ºC under Ar atmosphere with a temperature ramp rate of 20 ºC/min.
- The magnetization and magnetic susceptibility were measured with a Weiss-type magnetic balance in a temperature range of 300-800 K.

Electronic Structure Calculation Results:

Mn-Al system ⇒ ***Mn and Al atoms are situated in alternating planes*** spaced at a distance of $c/2$ [1].

Mn atoms situated in ***adjacent planes*** (Mn^{1a}-Mn^{2e} pairs) ⇒ ***AFM coupling.***

In order to ***decrease*** the weight of the ***AFM interactions*** ⇒ ***Ni or Ti substitutions*** for Mn in $Mn_{54}Al_{46}$.

Smaller Ni or Ti moments ⇒ ***increase*** of the ***total magnetic moment*** for $Mn_{50}Al_{46}M_4$ (M = Ni, Ti).

- ***Smaller total energy*** for a ***mixed*** 1*a* and 2*e* ***Ni occupancy*** than for an exclusive 2*e* Ni occupancy.
- ***A lower total energy*** was found for the alloy with the ***AFM coupled Mn^{1a}-Mn^{2e} pair.***

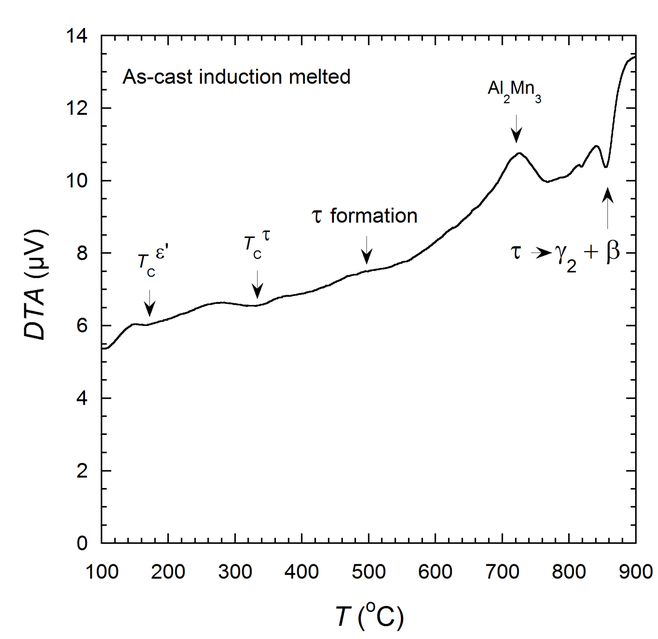
Calculated magnetic moments for the τ phase of $Mn_{50}Al_{46}M_4$(M = Ni, Ti), $Mn_{50}Al_{50}$ and $Mn_{54}Al_{46}$ alloys.

		Mn		Al		M		Total	
		$m_s(\mu_B)$	$m_l(\mu_B)$	$m_s(\mu_B)$	$m_l(\mu_B)$	$m_s(\mu_B)$	$m_l(\mu_B)$	$m_s(\mu_B)$	$m_l(\mu_B)$
$Mn_{50}Al_{50}$		2.41	0.04	-0.08	-	-	-	4.68	0.08
$Mn_{54}Al_{46}$ (FM)	Mn^{2e}	2.43	0.007	-0.08	-	-	-	5.02	0.07
	Mn^{1a}	2.39	0.04						
$Mn_{54}Al_{46}$ (AFM)	Mn^{2e}	-3.17	-0.01	-0.07	-	-	-	4.38	0.08
	Mn^{1a}	2.35	0.04						
$Mn_{50}Al_{46}Ti_4$		2.34	0.04	-0.08	-	-0.66	-0.004	4.43	0.07
$Mn_{50}Al_{46}Ni_4$		2.45	0.04	-0.08	-	0.63	0.06	4.85	0.08

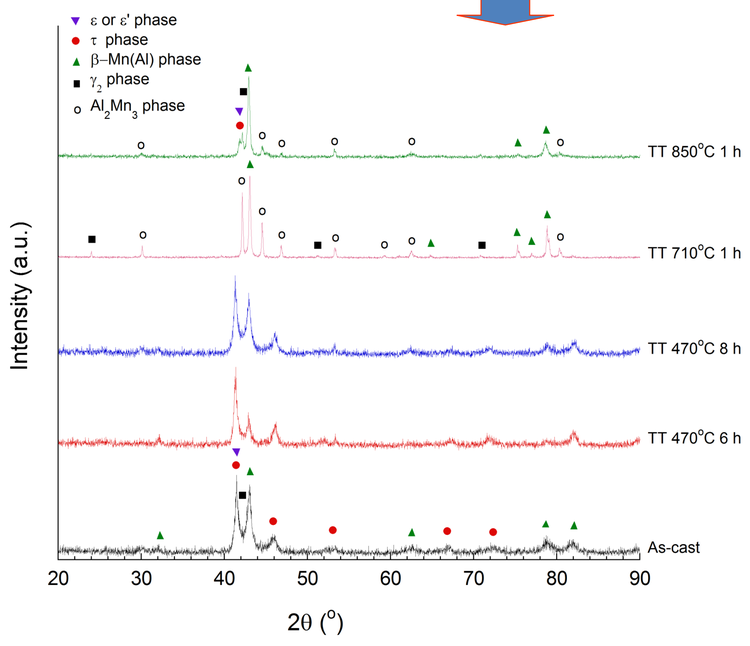
Experimental Results:

During the formation of the τ phase, the following transformation occurs [1,2]:
ε (disordered hexagonal) → ε' (ordered orthorhombic) → τ (tetragonal)

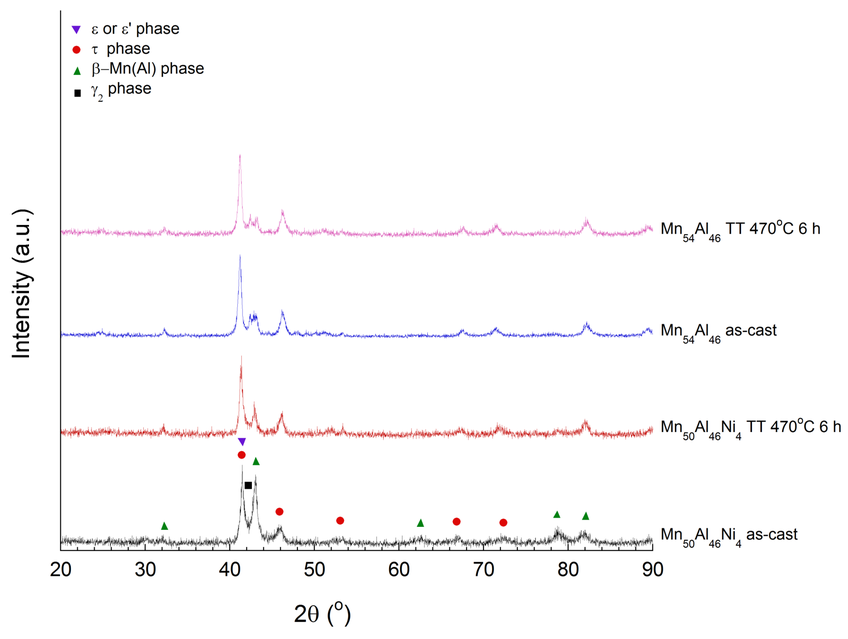
The ***ε' phase*** is an ***ordered ε phase*** [1,2] ⇒ ***XRD peaks*** of these two phases ***superimpose***.
Magnetic measurements can ***confirm*** whether the phase is ε or ε'.



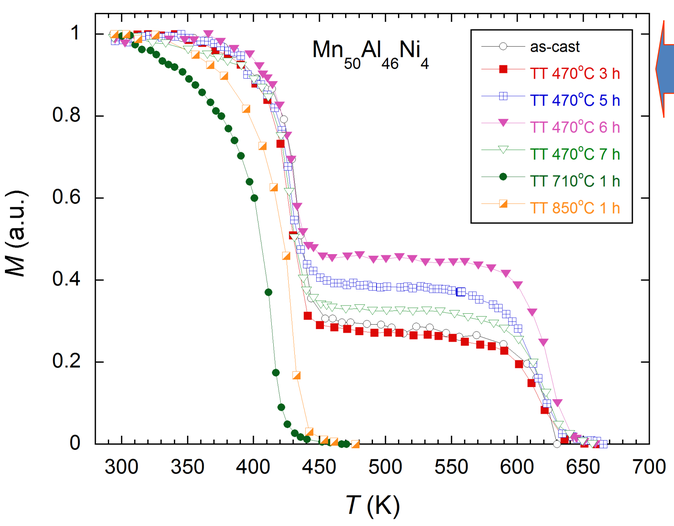
DTA curve for the as-cast $Mn_{50}Al_{46}Ni_4$ alloy.



XRD patterns for the $Mn_{50}Al_{46}Ni_4$ alloy after annealing at different temperatures.



XRD patterns for the as-cast and annealed $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ alloys.



Temperature dependence of the normalized magnetization of the $Mn_{50}Al_{46}Ni_4$ alloy after annealing at different temperatures.

As-cast + TT 470 ºC 6h

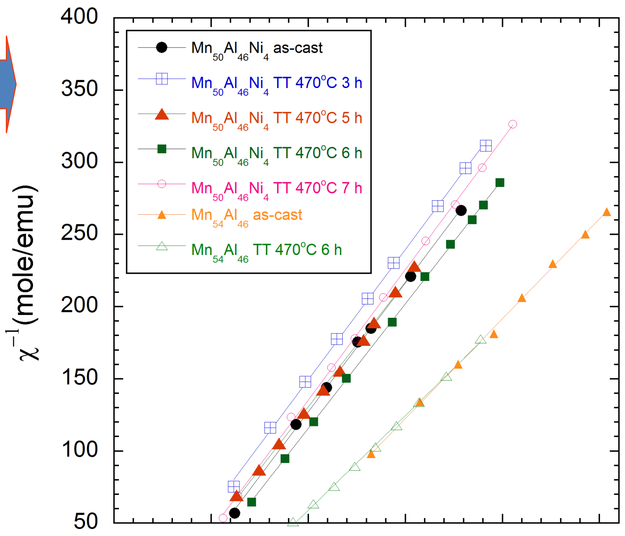
Two magnetic phases:
τ (hight T_c) and ε' (low T_c).

TT 710 ºC + 850 ºC

single magnetic phase behavior (lower T_c)

The experimental data fits the Curie-Weiss law $\chi = C/(T-\theta)$ with the parameters given in the table below.

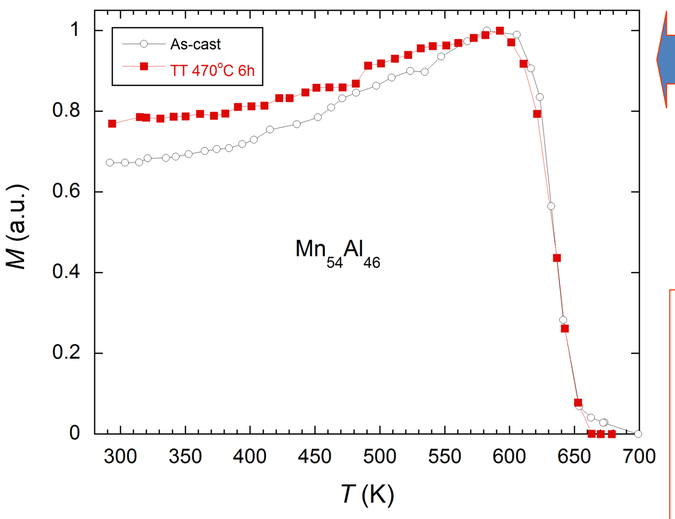
The average experimental Mn moment in the ordered state was calculated taking into account the concentrations $c_{\varepsilon'}$ and c_τ of the ε′ and τ phases and the theoretical values of Mn moments in the two phases ($\mu_{\varepsilon'}$ = 1.88 μ_B/Mn atom and μ_τ = 2.37 μ_B/Mn atom [1]) according to the relation: $\mu_{exp} = c_{\varepsilon'}\mu_{\varepsilon'} + c_\tau\mu_\tau$.



Reciprocal susceptibility versus temperature curves of the $Mn_{50}Al_{46}Ni_4$ and $Mn_{54}Al_{46}$ alloys. The lines represent the Curie-Weiss fit of the experimental data.

The μ_{eff} values, the Mn spins S, the τ phase content c_τ, the average Mn moments in the ordered state μ_{teor} and μ_{exp}, the paramagnetic Curie temperatures θ, and the Curie temperatures T_C, of the τ phase of the $Mn_{50}Al_{46}Ni_4$ and $Mn_{54}Al_{46}$ alloys.

Sample	μ_{eff}/f.u (μ_B)	μ_{eff} /Mn (μ_B)	S_{Mn}	c_τ (%)	μ_{teor} (μ_B)	μ_{exp} (μ_B)	θ (K)	T_C (K)
$Mn_{50}Al_{46}Ni_4$ as-cast	2.11	2.98	1.07	35	2.14	2.05	629	624
$Mn_{50}Al_{46}Ni_4$ TT 470 ºC 3 h	2.10	2.97	1.07	33	2.14	2.04	617	625
$Mn_{50}Al_{46}Ni_4$ TT 470 ºC 5 h	2.15	3.04	1.1	43	2.2	2.09	624	635
$Mn_{50}Al_{46}Ni_4$ TT 470 ºC 6 h	2.15	3.04	1.1	50	2.2	2.13	633	632
$Mn_{50}Al_{46}Ni_4$ TT 470 ºC 7 h	2.10	2.97	1.07	38	2.14	2.07	625	629
$Mn_{54}Al_{46}$ as-cast	2.40	3.27	1.21	100	2.42	2.37	662	643
$Mn_{54}Al_{46}$ TT 470 ºC 6 h	2.47	3.36	1.25	100	2.50	2.37	655	644



Temperature dependence of the normalized magnetization of the as-cast $Mn_{54}Al_{46}$ alloy and the sample annealed at 470° C for 6 h.

$Mn_{54}Al_{46}$ samples

single magnetic phase behavior (τ phase).

Close values of the μ_{teor} and μ_{exp} values ***confirm*** the existence of the ***ε′ and τ phases*** in the investigated $Mn_{50}Al_{46}Ni_4$ alloy.

Conclusions:

- The ***largest calculated*** magnetic ***moment*** was found for the ***$Mn_{50}Al_{46}Ni_4$*** alloy.
- A ***lower total energy*** was found for the alloy with the ***AFM coupled Mn^{1a}-Mn^{2e} pair.***
- All of the samples are phase mixtures and are ferromagnetic at room temperature. The ***τ phase was found along with the ε' phase*** only in the ***as-cast $Mn_{50}Al_{46}Ni_4$ sample*** and the ones ***annealed at 470 ºC*** with a ***maximum τ phase concentration of 50%.***
- ***Close values of the μ_{teor} and μ_{exp}*** values ***confirm the existence of the ε′ and τ phases*** in the investigated $Mn_{50}Al_{46}Ni_4$ alloy.
- Ongoing experimental work is currently being conducted to obtain the τ phase as a majority phase in these compounds.

[1] J. H. Park, Y. K. Hong, S. Bae, J. J. Lee, J. Jalli, G. S. Abo, N. Neveu, S. G. Kim, C. J. Choi, J. G. Lee, *J. Appl. Phys.*, **107**, 09A731 (2010).

[2] T. E. Prost, " PhD Thesis: Magnetic Properties Study of the Mn-Al System with Additions of B or C and Mechanical Milling Techniques", University of Nebraska – Lincoln, 2012.

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