Structural and Magnetic Properties of Mechanically Milled $Mn_{50}Al_{46}T_4$ (T = Mn, Ni) Alloys

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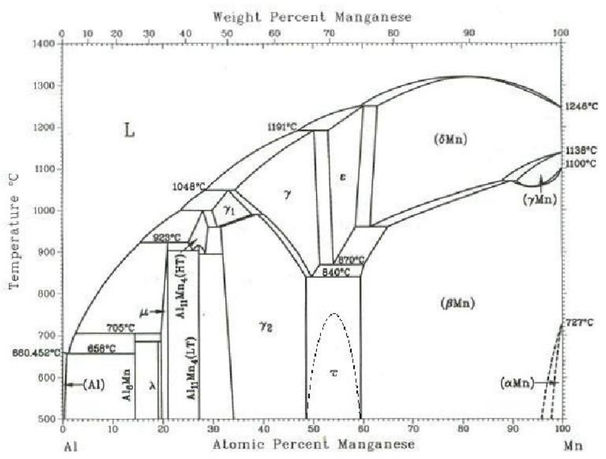
Abstract: The metastable τ-phase (tetragonal $L1_0$ structure) of the Mn-Al system was reported to have interesting magnetic properties for permanent magnet applications, the most stable composition being $Mn_{54}Al_{46}$. It was shown that the magnetic properties of the τ-phase can be improved through doping and mechanical milling (MM). In this work, the structural and magnetic properties of milled $Mn_{50}Al_{46}T_4$ (T = Mn, Ni) alloys were investigated. The as-cast samples were found to be phase mixtures. For T = Mn the τ-phase was the main phase, while for T = Ni the κ-phase (CsCl type structure) was a majority phase. Following annealing the 5 h MM samples were composed mainly of the τ-phase (T = Mn) and κ-phase (T = Ni) respectively. The best results were obtained for the 5 h MM annealed sample with T = Mn which showed significantly higher remanence and coercivity values than the as-milled samples.

Experimental Details:

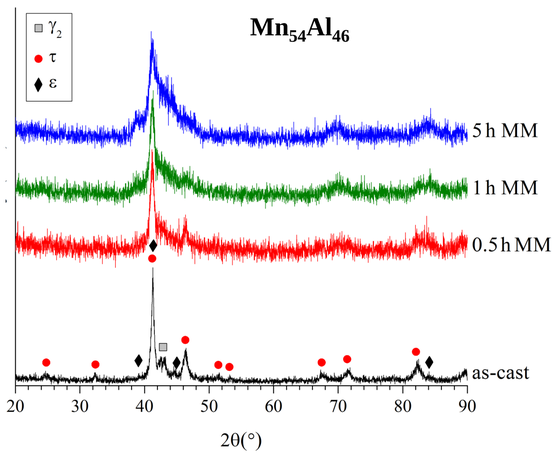
- The $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere.
- The samples were dry-milled in a Fritsch Pulverisette 4 planetary ball mill under Ar using Ø = 10 mm diameter balls for 0.5, 1 and 5 h. The milling vials (with a volume of 45 ml) and balls were made of 440C hardened steel. The ratio between the rotation speed of the disk and the relative rotation speed of the vials was Ω/ω=333/-900 rpm with a ball-to-powder weight ratio of 10:1.
- The samples (small quantity < 50 mg) were sealed in a silica tube and annealed in an inert Ar atmosphere at 1050ºC for 1 h followed by quenching in water.
- XRD investigations were performed using a Brüker D8 Advance X-ray diffractometer with Cu K_α radiation.
- Demagnetization curves were measured on a Cryogenics VSM at 300K after magnetization at 10 T.

Experimental Results:

$Mn_{54}Al_{46}$

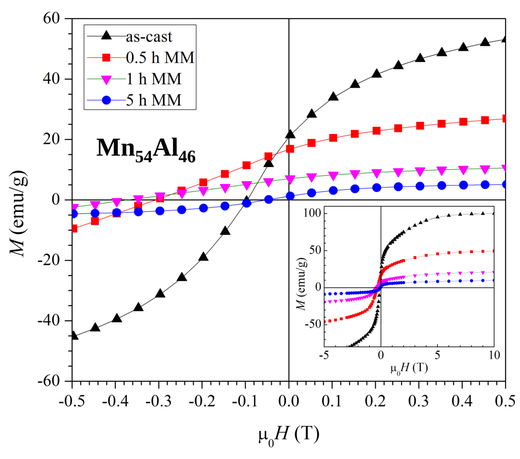


X-ray Diffraction Patterns



Coercivity increases from 0.12 T to 0.3 T after 0.5 h MM with only a small drop in remanence. Further milling leads to the destruction of the magnetic phase.

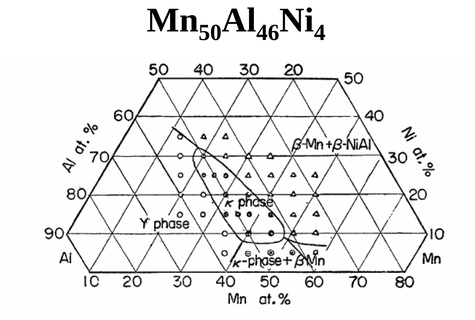
Demagnetization curves



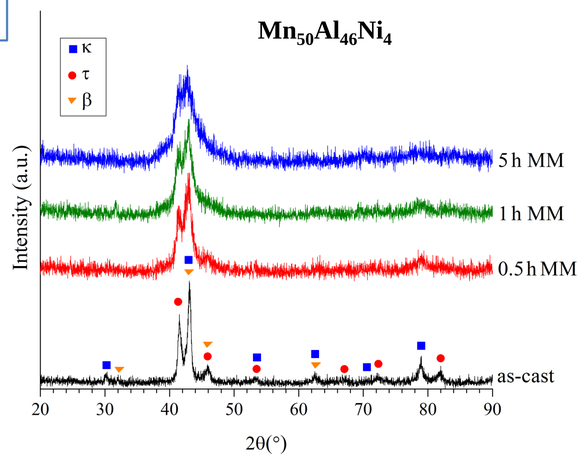
Due to the **damage induced to the $L1_0$ τ phase** after 5 h MM, the remanence and coercivity values are strongly diminished.

τ -phase → tetragonal $L1_0$ type structure, ferromagnetic [2]
ε -phase → hexagonal closed-packed, antiferromagnetic [2]
κ-phase → CsCl type structure, ferromagnetic [3]

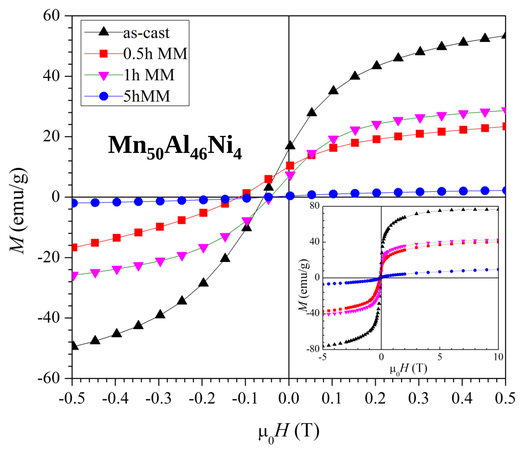
$Mn_{50}Al_{46}Ni_4$



Partial room temperature phase diagram of the **Mn-Al-Ni system** [3]



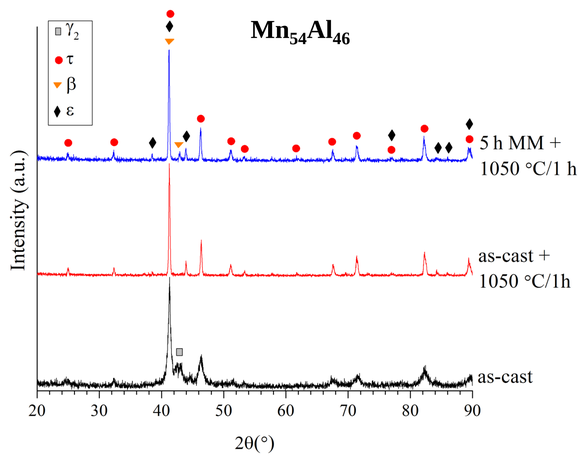
Coercivity increases from 0.06 T to 0.11 T after 0.5 h MM with a drop in remanence. Further milling leads to the destruction of the magnetic phase.



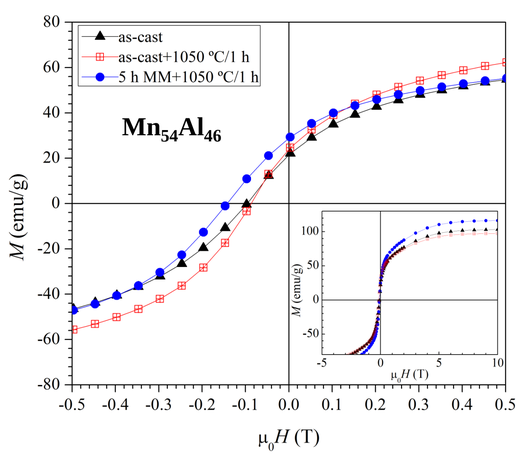
The lower coercivity and remanence in the case of the $Mn_{50}Al_{46}Ni_4$ sample is due to the presence of the **κ soft magnetic phase**

In order to refine the crystalline structure of the τ phase a <u>heat treatment (HT)</u> was performed for 1 h at 1050 ºC.
Rapid cooling from the ***ε region*** to ***obtain τ phase***

The **$Mn_{54}Al_{46}$** samples respond very well to the **heat treatment,** yielding a **majority τ phase** and sharp diffraction peaks.



Magnetic properties improved due to the significantly better **crystallinity of the τ phase**

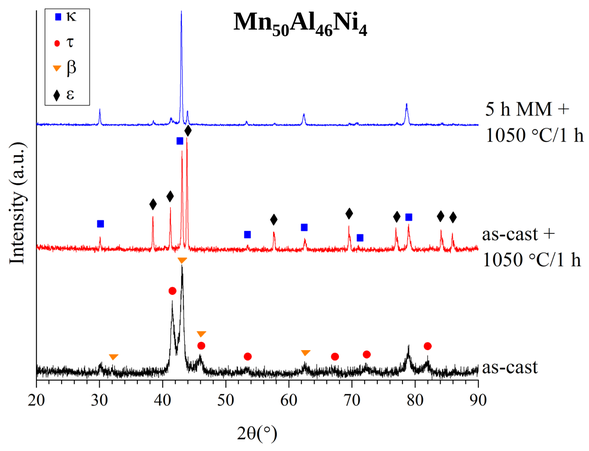


as-cast
$\mu_0 H_c$=0.1 T
M_r=22 emu/g

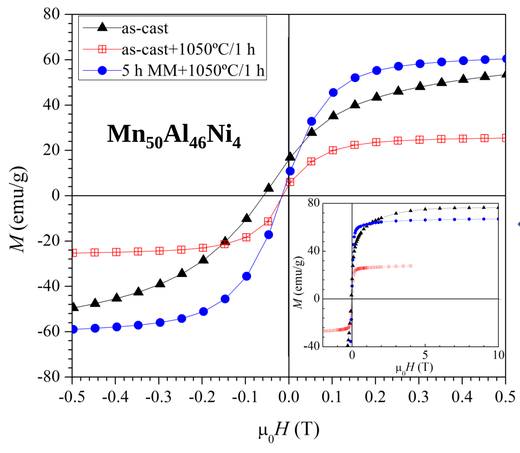
MM + HT

$\mu_0 H_c$=0.15 T
M_r=29 emu/g

XRD shows that **Ni addition** favors the formation of the soft magnetic **κ phase**



The **coercivity and remanence decrease** after heat treatment due to the significant **increase** in the concentration of the **soft magnetic κ phase**



Magnetic measurements **confirm** the formation of the **κ phase**

Conclusions:

- ***Mechanical milling*** increases coercivity in both the $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ samples for up to ***0.5 h MM***, longer milling times resulting in the destruction of the magnetic phase.
- ***Heat treatment*** yields very good results in the stabilization of the **τ phase for $Mn_{54}Al_{46}$** while in the case $Mn_{50}Al_{46}Ni_4$ it results in the formation of the **soft magnetic κ phase**.
- The ***mechanically milled and annealed*** sample of $Mn_{54}Al_{46}$ yielded the best results, ***featuring increases in both remanence (29 emu/g) and coercivity (0.15 T),*** compared to the as-cast sample.
- Even though the current annealing process produces good results, further ***refinement of the cooling rate*** could yield higher τ-phase concentrations for $Mn_{54}Al_{46}$.

[1] Park J H et al., *J. Appl. Phys.* **107** (2010) 09A731
[2] Tsuboya I et al., *J. Phys. Soc. Jpn.* **16** (1961) 1257
[3] Liu Z W et al., *J. Mat. Sci.* **47** (2011) 2333

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