Structural, electronic and magnetic properties of the Mn$_{54-x}$Al$_{46}$Ti$_x$ alloys

(\(x = 2; 4\) alloys)

R. Gavrea$^1$, R.Hirian$^1$, S. Mican$^1$, D. Benea$^1$, O. Ibanoae$^2$, 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$_{54}$Al$_{46}$Ti$_x$ and Mn$_{54}$Al$_{46}$Ti$_x$ 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\(\mu_B/\text{Ti}\)) coupled antiparallel relative to the Mn magnetic moments in the plane of Mn atoms (2.33\(\mu_B/\text{Mn}\)). The as-cast and annealed samples were phase mixtures with different values of the hard ferromagnetic \(\gamma\)-phase content. The ferromagnetic \(\gamma\)-phase was found along with the nonmagnetic \(\gamma\)-phase in the as-cast Mn$_{54}$Al$_{46}$Ti$_x$ alloy. Except the as-cast and annealed at 1050 °C for 1 h Mn$_{54}$Al$_{46}$Ti$_x$ alloys, all the analyzed samples pointed out the presence of a soft Mn-phase with a Mn magnetic moment close to that found in the \(\gamma\)-phase and with \(\gamma\)-content around 500 K. The best magnetic characteristics were obtained for Mn$_{54}$Al$_{46}$Ti$_x$ alloy annealed at 470 °C for 6 h; \(M=116 \text{ Am/Kg} /4 \text{ K}\) and \(T_c=160 \text{ K}\), in good agreement with the values reported in the literature for the \(\gamma\)-phase of the MnAl system. The increase of the Ti content from \(x = 2\) to \(x = 4\) in Mn$_{54}$Al$_{46}$Ti$_x$ leads to the decrease of the \(\gamma\)-phase content and consequently to the increase of the soft ferromagnetic \(\gamma\)-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$_{54}$Al$_{46}$Ti$_x$ and Mn$_{54}$Al$_{46}$Ti$_x$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere and annealed at 470 °C for 6 h and 1050 °C for 1 h.
- The high-purity Mn (99.95 wt%), Al (99.99 wt%) and Ti (99.99 wt%) were used as starting materials.
- XRD investigations were performed using a Bruker D8 Advance X-ray diffractometer with Cu K$_\alpha$ radiation.
- Magnetization measurements were performed using an extraction magnetometer in the temperature range 4–800 K 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:

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_c) (K)</th>
<th>(M) (Am$^2$/Kg)</th>
<th>(\mu_0H) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{54}$Al$</em>{46}$Ti$_2$ as cast</td>
<td>1050</td>
<td>116</td>
<td>0.1</td>
</tr>
<tr>
<td>Mn$<em>{54}$Al$</em>{46}$Ti$_2$ annealed</td>
<td>1050</td>
<td>120</td>
<td>0.1</td>
</tr>
</tbody>
</table>

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$^{4+}$ and Mn$^{6+}$ sites) are coupled antiparallel with the Mn magnetic moments in the Al plane (Mn$^{2+}$ sites).
- The smallest total energy of Mn$_{54}$Al$_{46}$Ti$_2$ and Mn$_{54}$Al$_{46}$Ti$_4$ was obtained for Ti atoms sitting on the 2\(\delta\) sites.

Magnetic Investigations:

- The Mn$_{54}$Al$_{46}$Ti$_2$ annealed at 470 °C for 6 h sample pointed out the presence of the soft \(\gamma\)-phase, although this phase was not observed in XRD investigations, probably due to the superposition with \(\gamma\)-phase.
- The soft \(\gamma\)-phase is present in all Mn$_{54}$Al$_{46}$Ti$_x$ alloys.
- The second transition may be attributed to the ferromagnetic-paramagnetic transition of the hard magnetic \(\gamma\)-phase of the Ti-doped samples.
- The increase of the Curie temperature for \(x = 4\) 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 \(\gamma\)-phase component in the majority of the investigated samples.

Conclusions:
- All the analyzed samples contain \(\gamma\) and \(\gamma\)-phases, but the Mn$_{54}$Al$_{46}$Ti$_x$ alloys contain along these two phases also the \(\kappa\)-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$_{54}$Al$_{46}$Ti$_x$ leads to the decrease of the \(\gamma\)-phase content and consequently to the increase of the soft ferromagnetic \(\gamma\)-phase.
- The values of the Curie temperatures \(T_c\) and \(T_c^{\kappa}\) of the as-cast and annealed Mn$_{54}$Al$_{46}$Ti$_2$ and Mn$_{54}$Al$_{46}$Ti$_4$ alloys suggest that the solubility limit of Ti in Mn$_{54}$Al$_{46}$Ti$_x$ is about 2%, in good agreement with the XRD results.

Acknowledgement
This work was supported by the Romanian Ministry of Education and Research, Grant No. PN-III-P1-11541/2013 and PN-II-P1-1169/2013-4-2560.