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Studies of CeMnAl and its Hydride

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Introduction

In contrast to the $CeAl_2$, which does not form hydrides, and Ce-Mn, which does not form binary intermetallic compounds, CeMnAl absorbs considerable amounts of hydrogen. The melting procedure for Ce-Mn-Al alloys is challenging due to the high vapor pressure of Mn at the melting point of the alloy.

Experimental

Samples were produced by r.f. levitation heating under a reduced argon atmosphere of 0.5 bar. In order to improve the homogeneity of the alloy lumps they were remelted three times. A large-scale sample (≈200 g) was produced by Gesellschaft für Elektrometallurgie, Nürnberg, Germany. For the diffraction measurements the samples were grounded mechanically in an Argon glove box to prevent oxide formation. X-ray diffraction was performed with a SIEMENS D500 MP diffractometer using Cu Kα radiation. For the neutron diffraction measurement at the high flux reactor in Grenoble (ILL), copper coated cylindrical vanadium sample holders were used.

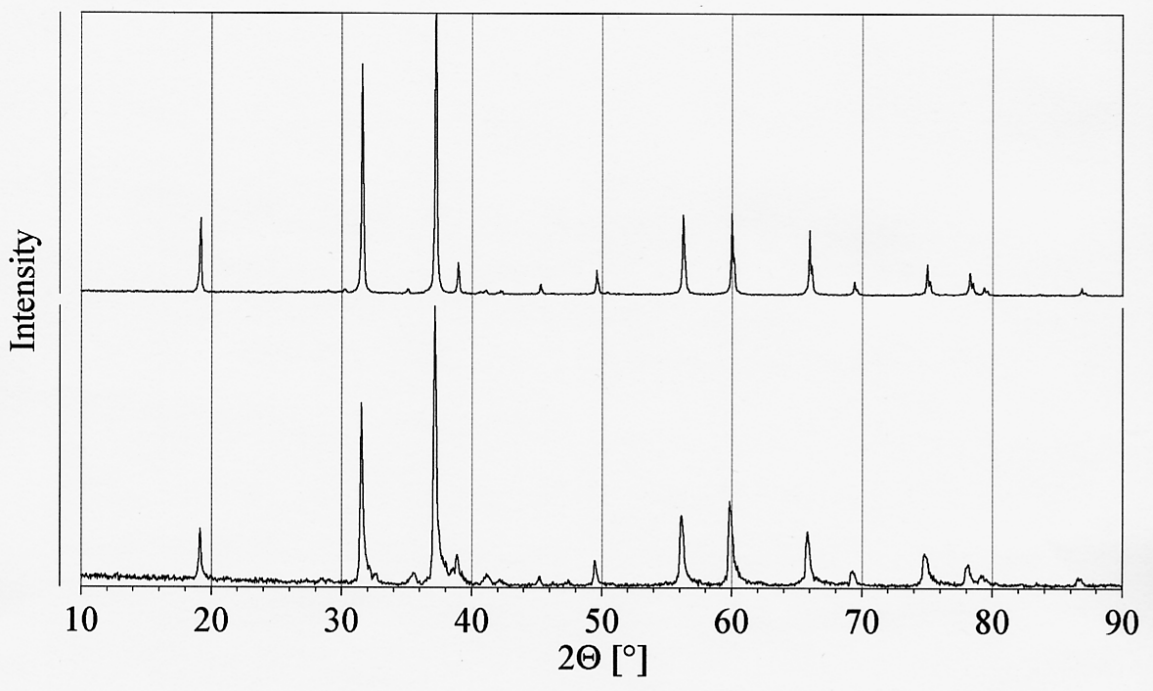

Figure 1 - X-Ray diffraction patterns of CeMnAl samples (as cast [bottom] and after annealing [top])

Results

The X-ray diffraction pattern of the CeMnAl alloy as cast and after annealing is shown in Figure 1. The crystalline quality was improved during the annealing procedure. The second phase, the presence of which is visible from a few minor peaks (especially the peak at 35°), was strongly reduced upon annealing. The major phase is the cubic C15 Laves phase. Ce occupies the A-sites and Mn and Al are distributed randomly on the B-sites.

CeMnAl absorbs hydrogen up to 2.4 H/f.u. (hydrogen-per-formula unit). A large amount (≈1.2 H/f.u.) of the hydrogen is absorbed at a pressure below 1 mbar. The hydrogen absorption curve is shown in Figure 2. The formation of the hydride phase occurs in the low-pressure range, as detected from the change of the lattice parameter. For pressures greater than 1 mbar, the lattice parameter increases with increasing hydrogen concentration.

Attempts were made to use the CeMnAl alloy as electrode material in an electrochemical cell. Unfortunately no hydrogen was absorbed. The alloy corroded within a few days in the 6 M KOH electrolyte. The main problem is that none of the elements in the alloy are electrochemically stable. Furthermore, there is no nickel in the alloy. Nickel is electrochemically stable in the applied potential range and has a high catalytic activity for the dissociation of water molecules.

Neutron diffraction measurement (Figure 3) of the CeMnAl alloy and its deuteride showed that the deuterium occupies only the 96g-sites (A_2B_2 tetrahedron). The calculated occupancies of the 96g-sites are in good agreement with the capacities determined from the prior constant deuterium gas-flow absorption/desorption measurement.

More details of this work can be found in [1].

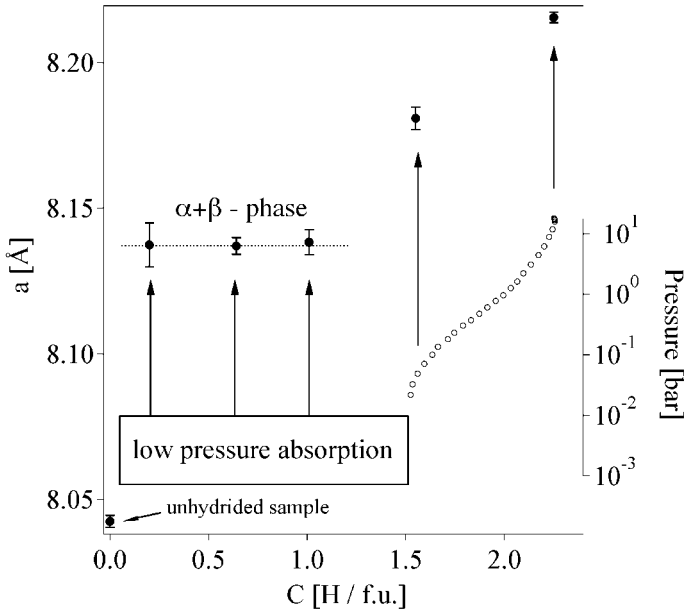

Figure 2 - The lattice parameter of the unit cell (left axis) as a function of the hydrogen content (hydrogen atoms per formula unit) in the cubic $CeMnAlH_x$ Laves-phase system. The corresponding absorption pressure is shown on the right axis. 1.2 H/f.u. are absorbed at low pressure.

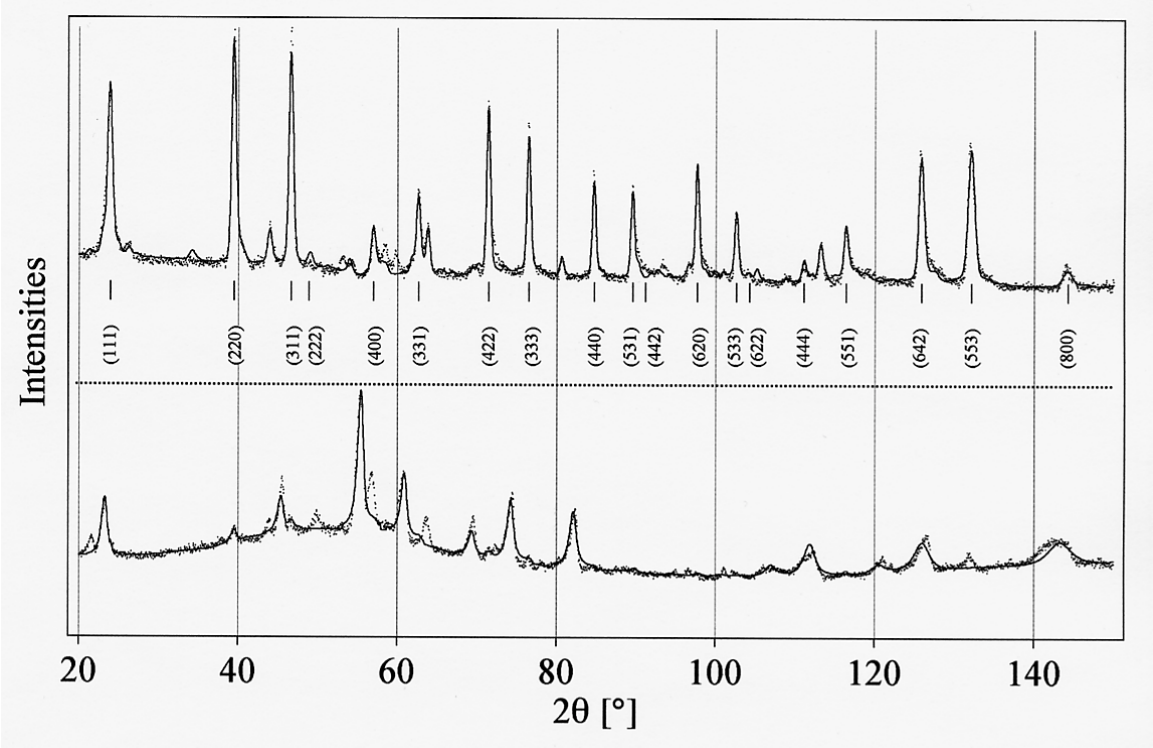

Figure 3 - Neutron diffraction pattern of Ce(MnAl) alloy (on top) and Ce(MnAl)D_x (on bottom)

Outlook

The Ce(MnAl) alloys exhibit a rather large hydrogen absorption at a hydrogen pressure below 1 mbar. This property allows one to use the Ce-Mn-Al intermetallic as getters.

Reference

[1] P. Spatz, K. Gross, A. Züttel, F. Fauth, P. Fischer and L. Schlapbach: "$CeMnAlH_x$, a New Metal Hydride", J. Alloys and Compounds, **261** (1997) 263-268