Hydrogen Absorption in YNi_4Mn, an Alloy with the Cubic UNi_5 Structure

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Summary For the first time, reversible hydrogen absorption and desorption has been observed in an alloy, YNi_4Mn, with the cubic UNi_5 structure, rather than in the well known AB_5 alloys having the hexagonal $CaCu_5$

structure which are of importance for hydrogen storage applications.

UP to now, all alloys of general composition AB_5 which have been found reversibly to absorb and desorb large quantities of hydrogen have had the hexagonal $CaCu_5$ type structure. YNi_4Mn has been shown to crystallize with the cubic UNi_5 type structure.[1] Recently, we have been able to activate the alloy YNi_4Mn and to observe for the first time rapid hydrogen absorption and desorption in an alloy of this structure.

The YNi_4Mn alloy, prepared by standard arc melting procedures, was found by *X*-ray powder diffraction to be cubic with $a = 6{\cdot}972$ Å. It had been reported earlier that YNi_4Mn could not be activated by exposure to hydrogen at pressures up to 1000 lb in^{-2}.[2] We have activated the alloy by cooling it to 0 °C and then exposing to *ca.* 1500 lb in^{-2} of hydrogen. After standing overnight, the absorbed hydrogen was removed by pumping at room temperature. At pressures of 1200 lb in^{-2}, the composition of the hydride approached $YNi_4MnH_{4\cdot5}$. There is apparently a rather extended solid solution region for hydrogen in the β-phase hydride as the plateau extended only to the composition $YNi_4MnH_{1\cdot8} \pm {}_{0\cdot2}$. The constant pressure plateau region is considerably shorter than, for example, in the case of $LaNi_5$ where it extends approximately to the composition $LaNi_5H_{5\cdot6}$. The extended β-phase solid solution range is presumably characteristic of hydrides derived from the cubic UNi_5 structure. The hydrogen dissociation pressure near the middle of the plateau ($H = 1{\cdot}0$) was *ca.* 5·6 lb in^{-2} at 21 °C. After four hydriding–dehydriding cycles, the sample changed to a powder, whose *X*-ray diffraction pattern, however, was identical with that of the original material. In another experiment, the hydride form of the alloy was transferred without special precaution to an *X*-ray capillary. The powder *X*-ray diffraction pattern indicated that most of the hydrogen had desorbed from the sample since many of the observed lines were the same as for the alloy. However, two new weak lines corresponding to the two strongest alloy lines, but shifted to larger *d*-spacings, were also observed. From these two lines, the hydride structure was deduced to be cubic with lattice parameter estimated to be $a = 7{\cdot}3$ Å. This conclusion is tentative since it is based on very limited data.

An objective of the present series of studies is to correlate the structural and thermodynamic properties of the AB_5 hydrides. The hydrides based on cubic AB_5 alloys present a new class of materials whose thermodynamic properties, such as their entropies of transition, may be compared with the configurational entropies of the hydrides based on the hexagonal AB_5 alloys.[3] The YNi_4Mn hydride does not follow the cell volume–dissociation pressure correlation established for the hexagonal AB_5 hydrides.[4] It remains to be determined whether the anamolous behaviour is associated with change in structure.

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