MECHANOCHEMICAL SYNTHESIS OF Mg-Co HYDROGEN ABSORBING PHASES

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Introduction

Magnesium and magnesium-based alloys are well known materials for hydrogen storage. However, in magnesium-based systems there are very few intermetallic compounds absorbing hydrogen reversibly without decomposition. As a rule, only Mg_2Ni was regarded as a candidate for practical application. One of the possible explanations of this fact may be immiscibility of magnesium with a large number of elements of periodic system, in particular with many transition metals. It makes difficult but not impossible searching new magnesium-based systems for hydrogen storage. For example, it was shown that hydriding (at definite experimental conditions) of mixture of immiscible Mg and Fe led to the formation of ternary hydride Mg_2FeH_6 [1,2]. Two ternary hydrides and one intermetallic compound were found in the case of Mg and Co [3,4] in spite of the absence of hydride forming intermetallic compound in magnesium-cobalt equilibrium phase diagram. These ternary hydrides proved to be thermally more stable than MgH_2, but they possess higher hydrogen capacity than Mg_2NiH_4 and very high hydrogen density by volume (more than $7 \cdot 10^{22}$ atoms H/cm^3).

For achieving reasonable rate of formation and relatively high yield of magnesium-cobalt ternary hydrides very fine mixture of metal powders is necessary.

Mechanical alloying (MA) is known not only as method for preparing fine composites of two or more components but also as nonequilibrium process leading to formation of metastable products often possessing unusual properties.

In this study, the high energy mechanical alloying of magnesium and cobalt in atomic relation 2Mg:Co under argon or hydrogen atmosphere and the reactivity of products toward hydrogen have been investigated.

Results and discussion

Mechanical alloying was carried out with a high-energy planetary centrifugal mill of the AGO-2 type (acceleration about 40 m$\cdot$s^{-2}). Stainless steel vials and balls of 5 mm in diameter were used. After loading the samples, the vials were evacuated and filled with argon or a mixture of argon and hydrogen. The filling of the vials with gases was repeated periodically during process.

It has been shown [4] that the magnesium-cobalt mechanical alloys formed at initial stages of MA (for 5 min) react with hydrogen at elevated temperatures even at hydrogen pressures below the equilibrium pressure of MgH_2, with ternary hydrides being formed. The process and results of longer mechanical alloying have been established to depend considerably on gaseous atmosphere used. The gradual powdering of metals took place under argon atmosphere whereas the process similar to self-propagating high-temperature synthesis (SHS) had been observed in the case of hydrogen. Fig.1 presents the X-ray diffraction patterns of the samples obtained as a result of mechanical alloying magnesium and cobalt powders under hydrogen atmosphere for different time.

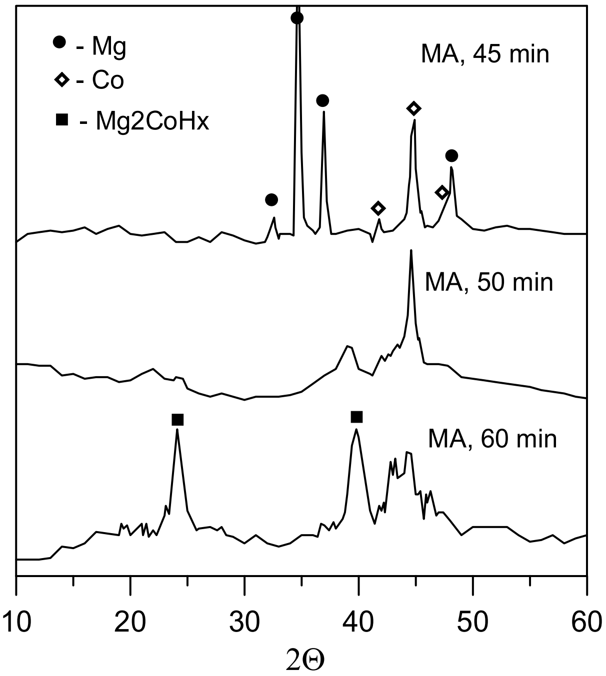

Fig.1. X-ray diffraction patterns of mechanically alloyed 2Mg+Co samples. The initial partial hydrogen pressure was about 4.5 atm.

First 45 minutes of mechanical alloying did not lead to formation any new compounds. All X-ray diffraction peaks belongs to magnesium or cobalt phases. But after subsequent 5 minutes of MA the picture changed drastically. With the exception of one peak at $2\theta=44^0$ attributed to cobalt phase, only two haloes were observed in the X-ray diffraction pattern of the sample obtained for 50 min MA.

Then the rapid formation of Mg_2CoH_5 ternary hydride took place (60 min of MA).

This phenomenon may be explained if one takes into account the exothermic character and the possibility of formation of magnesium-cobalt ternary hydrides directly from magnesium, cobalt and hydrogen [4]. The mechanical alloying of magnesium and cobalt powders in hydrogen atmosphere leads to mutual comminution of metals, creation of large Mg/Co interface and hydrogen adsorption on this interface. When the magnitude of interface and the concentration of adsorbed hydrogen reach the definite values the exothermic reaction begins. The heat being evolved leads to "ignition" of rapid self-sustaining reaction in all volume of composite.

The product formed as a result of SHS-like process contains hydrogen and seems not to be a mixture of phases. Only one rather broad peak can be observed on DTA curve at its decomposition (Fig. 2). More probably this product is an amorphous phase containing hydrogen in various positions with different bonding energy.

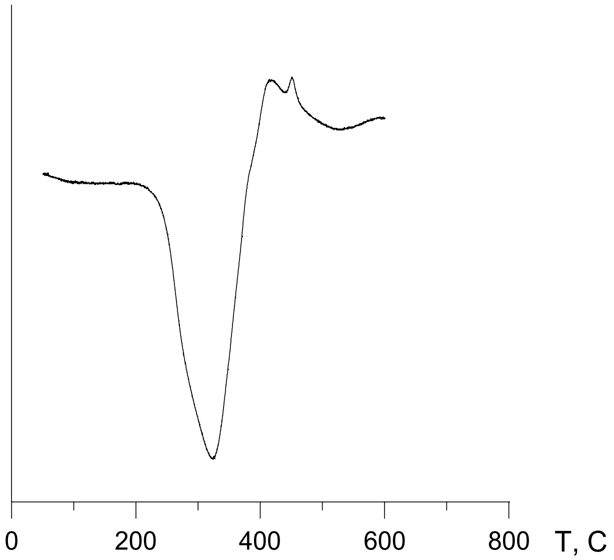

Fig.2. DTA curve of 2Mg+Co sample mechanically alloyed in hydrogen atmosphere at acceleration 40g for 50 min.

It should be noted that this phase begins to desorb hydrogen at about 230^0C which is lower then the temperature of MgH_2 or Mg_2CoH_5 decomposition.

Subsequent absorption of hydrogen by this phase both in the course of MA or separate hydriding leads to the formation of Mg_2CoH_5 hydride. The cubic Mg_2Co intermetallic compound is formed as a result of decomposition both intermediate amorphous and Mg_2CoH_5 phases. This intermetallic compound is able to absorb hydrogen at room temperature with the formation of solid solutions Mg_2CoH_x (x~1.5 at P=1.6 MPa) and at elevated temperatures with the formation magnesium-cobalt ternary hydrides.

Conclusions

The high energy mechanical alloying of magnesium and cobalt under argon or hydrogen atmosphere leads at initial stages to the formation of composites (mechanical alloys) which are able to react with hydrogen at elevated temperature even at hydrogen pressures below the equilibrium pressure of MgH_2, with ternary hydrides being formed.

The process similar to self-propagating high-temperature synthesis (SHS) has been observed in the case of hydrogen atmosphere at prolonged mechanical alloying.

The intermediate hydrogen-containing phase was formed as the result of SHS-like process. Subsequent absorption of hydrogen by this phase both in the course of MA or separate hydriding leads to the formation of Mg_2CoH_5 hydride. The intermediate phase begins to desorb hydrogen at about 230^0C with crystallisation of Mg_2Co intermetallic compound, which is able to reabsorb hydrogen at room temperature with the formation of solid solutions and at elevated temperatures with the formation magnesium-cobalt ternary hydrides.

References

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