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Hydrogen sorption properties of nanostructured bulk Mg_2Ni intermetallic compound

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ABSTRACT

Nanocrystalline Mg_2Ni intermetallic compound was produced from elemental components by induction melting and subsequent mechanical alloying in a planetary ball mill. Then the powder was compacted into bulk samples keeping the nanocrystalline structure. Hydrogen storage capacity of the Mg_2Ni bulk samples was found to be of about 1.9 wt.%. The absorption isotherm had a long plateau, corresponding to pressure of 0.1 MPa at the temperature of 553 K. The bulk samples demonstrated high durability after 21 absorption–desorption cycles.

1. Introduction

Among hydride forming alloys, applicable for reversible storage of hydrogen, special attention should be paid to the intermetallic compound (IMC) Mg_2Ni, combining high hydrogen-sorption capacity and relatively low cost. As a rule, such alloys obtained by metallurgical methods, have a macrocrystalline structure which requires difficult activation procedures for initiating sorption process. Usually, Mg_2Ni activation procedure includes conducting of 10–20 cycles sorption–desorption procedures, after which the pounding of the material and formation of metallic surface take place [1]. Moreover, using mechanical alloying (MA) it is possible to achieve a nanocrystalline structure and simplify or exclude the activation procedures for initialization of the absorption process [2,3]. In addition, as it was shown in the works [4,5], mechanical alloying of powder mixtures of Mg and Ni produced nanocrystalline intermetallic compound Mg_2Ni particles with crystallite sizes of 20–30 nm. This material reacts rapidly with hydrogen, and repeatability rate of hydrogenation is achieved in the second cycle. Also, the reaction rate and the amount of hydrogen absorbed increases with increasing the duration of mechanical alloying (MA) treatment, due to the local pounding of the sample and the appearance of a pure metal surface during this treatment [6]. Thus, one of the methods of improving the hydrogen sorption characteristics of metallic alloys is solid-phase mechanical alloying. The process of obtaining amorphous (or nanocrystalline) materials by MA has been actively studied for over 20 years [7–11] including MA of Mg_2Ni alloys [12–17].

Also, it should be noted, that mechanical activation process may take place during MA. It means accumulation of energy inside the crystals in the form of different defects, or other structural changes in the solid material, which reduce the activation energy for further chemical transformations of material, or improves conditions for the interaction processes [18,19].

One of the main problems of the powder hydrogen storage alloys is to prevent their flammability and improve the kinetics of hydrogen interaction. Compaction of bulk samples should improve heat, gas transfer kinetics and hydrogen absorption–desorption kinetics of powders.

In our previous works we evaluated enthalpy (accumulation energy) of the TiFe alloys prepared by MA [20] and performed subsequent compaction of these alloys prepared by MA [21,22].

However, in the literature there is not so much information about the preparation of bulk samples from MA Mg-based hydrogen storage alloys. The main problem is the destruction of the bulk samples during absorption–desorption processes. But, in spite of that, there are some successful research reports concerning the bulk hydrogen storage materials. For example, one of these papers on the production of Mg_2Ni bulky alloy by isothermal evaporation casting process [23], but these Mg_2Ni bulk alloys need various activation cycles to be applied for achieving saturated absorption capacity and hydrogen sorption stability. Also, there are some works reporting on the bulk samples of Mg-based alloys, also Mg_2Ni alloy, produced by bulk mechanical activation method [24–27]. The idea is based on the repeating forging processes (for several times) (Compaction-Withdrawal–Extrusion–Compaction–Withdrawal–Ejection–Compaction) [24], that makes possible to obtain the structures with high density of the crystalline defects (as at MA)

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in bulk samples. These bulk samples have good durability for the absorption–desorption cycles and exhibit the formation of a nanostructure to improve the activation process.

As it was shown in the works [28–31], Mg-based samples processed by ECAP (equal channel angular pressing) demonstrate improved hydrogen absorption properties.

In the work [32] the authors explained preparation of MgH_2 based powder alloys by mechanical alloying and subsequent SPS process. Also, in this work it was shown, that the bulk samples should be preferable in comparison with powder from the viewpoint of hydriding and de-hydriding kinetics.

That is why, for achieving good stability in hydriding and dehydriding kinetics and good durability during a large number of absorption/desorption cycles, the bulk samples of hydrogen storage alloys should have a sponge-type microstructure. Hydrogen atoms must be able to freely leak through these samples. These samples also must have a good thermal diffusivity and must be mechanically stable during hydrogen absorption–desorption processes. Such a kind of sponge samples are possible to be prepared by mechanical alloying and subsequent compaction with low-temperature sintering, as was shown in our previous works [21,22]. And, for example, such kind of the sponge-like samples prepared by nanoparticle consolidation, are similar to Pd hydrogen sorption alloys [33].

Therefore, in the present work interaction with hydrogen of the single-phase Mg_2Ni intermetallic compound samples produced from elemental components by induction melting and subsequent mechanical alloying in a planetary ball mill was studied. A technology for compacting Mg_2Ni intermetallic powder into bulk samples, with saving nanostructure (attained during MA process) and good durability was also developed.

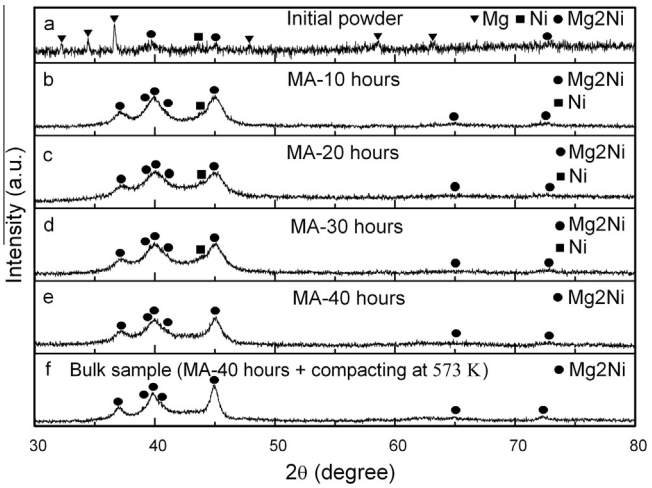

Fig. 1. XRD patterns of the Mg–Ni powder alloy: (a) powder mixture before MA; (b) after 10 h of MA; (c) after 20 h of MA; (d) after 30 h of MA; (e) after 40 h of MA; and (f) Mg_2Ni bulk sample after compacting and annealing.

2. Experimental details

The ingots of the Mg_2Ni alloys were prepared by induction melting method from the mixtures of pure metals (Mg and Ni) of 99.9 mass% purity in an argon atmosphere in boron nitride crucible. Atomic ratio of the mixtures employed was Mg/Ni = 67/33, i.e. Mg – 33 at.% Ni. The ingots of the Mg – 33% Ni (at.) prepared by induction melting were crushed to powder and exposed to MA treatment.

The mechanical alloying process was performed in a "Retsch" high energy planetary ball mill. The powder mixture was treated in an argon atmosphere for 40 h at a rotation speed of 400 rpm. The vials and milling balls (10 mm in diameter) made of stainless steel were used. The ratio of the mass of the balls and powder put in the drum was 10/1.

The structure of the prepared powder was examined by X-ray diffractometry with monochromatic CuKα radiation and scanning electron microscopy (SEM) carried out at 15 kV. The thermal analysis was performed using an "Exstar DSC 6300 SII" differential scanning calorimeter (DSC). DSC scans were performed in flowing argon on heating to 573 K at a rate of 20 K/min (weight of the sample was 30 mg).

Compaction of mechanically treated powders was performed in a TECAP APVM-904 laboratory pressing machine with subsequent heating in vacuum (10^{-5} torr) at 573 K for 10 min.

Thermal diffusivity analysis was carried out using the Netzsch LFA 447 NanoFlash. The temperature range of the analysis was from room temperature to 573 K.

The study of the interaction of the materials with hydrogen was carried out in a steel reactor in "Lesca" PCT-A04-01 machine, using an original experimental Sievert's type unit for precise p–v–T measurements under high pressure hydrogen atmosphere.

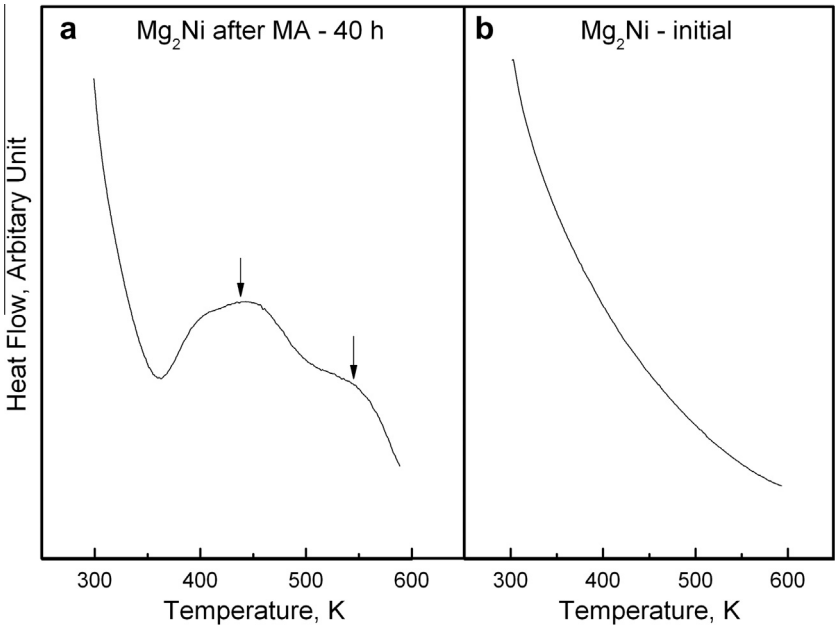

Fig. 2. DSC curves of Mg_2Ni sample prepared by MA for 40 h (a) and by induction melting (b).