

The synthesis of nanocrystalline Mg-Ni alloys for hydrogen storage

E. ENESCU, P. LUNGU, I. PASUK, G. STOIAN

National Institute for Research and Development in Electrical Engineering, Bucharest, Romania

The elaboration of nanocrystalline Mg-Ni alloys by mechanical alloying method is described. The ball milling was followed by a thermal treatment for recrystallization of amorphous powders. For improving the storage properties of the Mg₂Ni compound we used additions of metallic oxides like catalysts (V₂O₅, TiO₂). The obtained materials were characterised by XRD and SEM. The influence of processing parameters (atmosphere, milling time) on grain size evolution and milling efficiency is discussed. The results of some preliminary experiments of hydruation are presented.

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1. Introduction

Hydrogen is the ideal future energy carrier to substitute fossil fuels in the transportation sector and to serve in novel portable and stationary energy conversion systems. Among various ways of hydrogen storage, metallic hydrides have the advantages of relatively small volume, low pressure and safety. The Mg-based intermetallic compounds have attracted special attention as potential hydrogen storage materials because of the high reversible storage capacity of Mg, low weight and rich natural resources. However, its high thermodynamic stability limits the practical application. It is well known that the reaction kinetics of Mg can be improved by additions of transition elements (Zr, Ti, V, Fe) [1, 2] and transition metal (V, Ti, Cr, Mn) oxides [3,4].

The most studied Mg-based alloy is the A₂B-type Mg₂Ni intermetallic compound due to its low specific weight and cost. For its elaboration several fabrication techniques were developed. In the last time mechanical alloying was found to be a promising method for synthesizing novel hydrogen storage materials, including Mg-based alloys. It is realised by ball milling in a planetary mill or an attritor. During ball milling the initial powders are heavily deformed and thus repeatedly cold-welded and fractured. In this way, the microstructure is continuously refined and finally a chemically and microstructurally homogeneous material is achieved [5]. It contains a large amount of amorphous phase which, during subsequent annealing, form nanocrystalline grains. The nanostructured alloys reveal improved hydriding properties, mainly due to the large volume fraction of the grain-boundary regions [6].

2. Experimental

Pure powders of magnesium, nickel, TiO₂ and V₂O₅ were used as starting materials. The Mg and Ni powders were weighed in the atomic proportion of 2:1,

corresponding to the Mg₂Ni compound. Two mixtures were elaborated with 0.2 % mol TiO₂ and with 0.2 % mol V₂O₅. The Mg, TiO₂ and V₂O₅ powders were of micron size (< 40 μm) and the Ni powder of submicron size (approx. 200 nm estimated by XRD). The ball milling was performed with a planetary mill, with rotation velocity of 300 rot./min. and ball to powder mass ratio of 10:1. The tanks and balls were made from stainless steel. Initially was performed a dry milling under argon atmosphere, but after 30 hours of milling the powder began to agglomerate and stick on the tank's walls; then it was necessary to perform a wet milling in petroleum ether. Small samples of the powder were periodically taken from the mill at regular intervals of time. After drying in Ar atmosphere, their structure was studied by X-ray diffraction (BRUKER-AXS model D8 ADVANCE), using CuK_α radiation and k_β Ni filter, at 40 kV and 30 mA.

The powders milled for 50 and, respectively, 45 hours were thermally treated at 400 °C for 1 h under Ar atmosphere. The microstructure of the amorphous and recrystallized nanocomposites was examined by scanning electron microscopy.

The recrystallized powders were subjected to hydruation experiments at 150 °C temperature and 30 barr H₂ pressure.

3. Results and discussion

The effect of mechanical alloying processing is illustrated in the Fig. 1 by the XRD patterns of 2Mg+Ni – TiO₂ mixture at increasing milling times. The originally diffraction lines of component powders gradually became broader until they totally flattened in the amorphous state; this is the case of the Mg powder after 50 hours of milling.

From Fig. 2 it can be observed that the milling efficiency is greater for Mg than for Ni powder; thus, after 30 hours of milling the Mg crystallites became smaller than those of Ni and after 50 hours the Mg structure has disappeared while the Ni structure is still persisting as

independent phase with aprox. 50 nm crystallites. The particles average sizes were calculated with the Scherrer formula using the total width of the lines.

The TiO_2 nanoparticles containing a higher density of defects in the crystal structure after mechanical milling can absorb hydrogen and act as catalyst to improve the hydriding alloys properties [3]. Also, during the hydrogen desorption process, the TiO_2 nanoparticles decrease the stability of the hydride, indicating that the alloy can release H_2 at lower temperature. The specific TiO_2 lines did not appear in any XRD pattern, probably because of small quantity used (0.15 wt %).

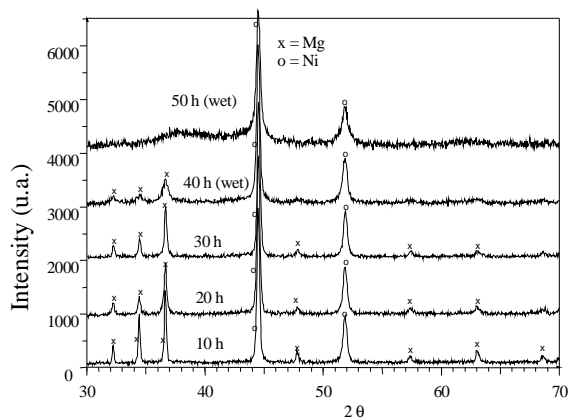


Fig. 1. XRD patterns of $2\text{Mg}+\text{Ni}-\text{TiO}_2$ after different milling times.

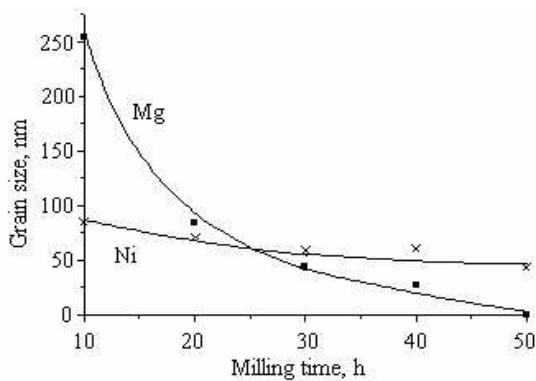


Fig. 2. Grain size evolution of Mg and Ni powders vs milling time.

After the thermal treatment of the amorphous powder the XRD pattern (Fig. 3) has evidenced the formation of Mg_2Ni nanocrystalline compound. Its main diffraction peaks correspond approximately to the diffused peaks from the pattern of the initial materials. This suggest that, after 50 hours, the milled material shows the presence of the crystal germs of the Mg_2Ni compound having nanometric dimensions.

The microstructural aspect of the nanocomposites before and after recrystallization treatment is presented in the Fig. 4.

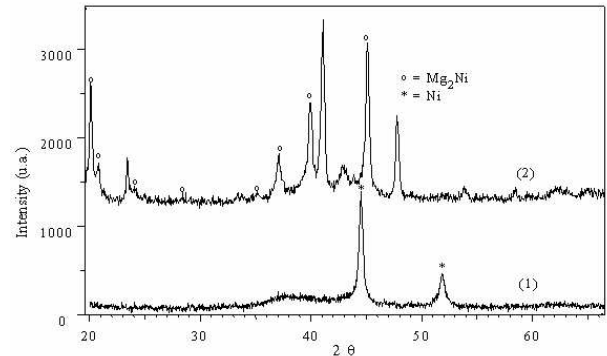


Fig. 3. XRD patterns of $\text{Mg}_2\text{Ni}-\text{TiO}_2$ nanocomposite in (1) amorphous and (2) recrystallized state.

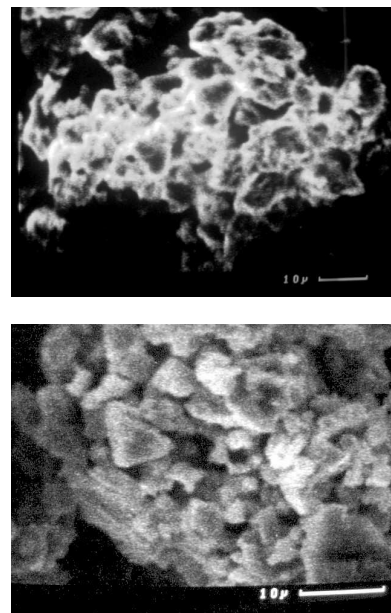


Fig. 4. SEM microstructural aspect of $\text{Mg}_2\text{Ni}-\text{TiO}_2$ nanocomposite in (1) amorphous and (2) recrystallized state.

Regarding the mixture with V_2O_5 addition, the XRD patterns at different milling times showed that after 15 hours of milling a amorphous phase was already formed, while the characteristics pattern for Mg disappeared. The diffused peaks of the amorphous phase correspond approximately to the most intense lines of the Mg_2Ni crystalline compound. This suggest that after 15 hours, the crystal germs of the Mg_2Ni compound were formed in the milled material. This behaviour may be connected with the V_2O_5 addition, although the specific V_2O_5 lines did not appeared in any XRD pattern, similarly as in samples with TiO_2 addition.

However, the subsequent milling of the mixture has led to the reappearance of the Mg and Ni independent crystalline phases. Only after 45 hours of milling begun to form again the amorphous phase of mechanically alloyed Mg and Ni powders, which by annealing treatment gives the Mg₂Ni nanocrystalline compound, similarly with the behaviour of the mixture containing TiO₂ addition.

The hydration experiments performed on the recrystallized powders at 150 °C and 30 barr H₂ showed for the Mg₂Ni-TiO₂ composite an absorption capacity of 2,5 % wt H₂ and for Mg₂Ni-V₂O₅ composite of 3.1 % wt H₂, after one absorption/desorption cycle and 30 minutes of hydration.

5. Conclusions

The Mg₂Ni nanocomposite compound was synthesized by mechanical alloying with additions of TiO₂ and V₂O₅ as hydriding catalysts. The component powders were ball milled and the time to reach almost full amorphization was determined. The wet milling was proved more efficient than the dry one, avoiding the stonning and oxidation of powders.

The amorphous alloys were annealed at medium temperature and transformed in nanocrystalline state with size of crystallites smaller than 50 nm. The hydrogen absorption capacity can be improved by raising the temperature and hydrogen pressure of hydration and by changing the processing parameters of the nanocomposite powders elaboration (milling time and speed, addition quantities etc).

References

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*Corresponding author: enescu@icpe-ca.ro