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Hydrogen Storage in Melt-spun Nanocrystalline Mg-Ni-Y Alloys

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1 Introduction

Magnesium-rich alloys are attractive materials for the reversible solid-state storage of hydrogen due to high gravimetric hydrogen storage densities that can reach up to more than five weight percent [1]. Further, Mg alloys are suitable for commercial use because of their cycle stability, their high abundance and the moderate cost of Mg as lightweight base material. However, the very slow hydrogen sorption kinetics of common bulk material requires strong improvement in view of practical applications. In the past decade, much attention has been devoted to the research and development of Mg alloys for hydrogen storage. It is now well established that, in order to improve the hydrogen sorption kinetics, magnesium alloys ought to possess a sub-micrometer crystal structure and should contain highly disperse catalyst particles [2]. For this purpose, Mg alloys can be ground by high-energy ball-milling techniques to reduce the average grain size and to disperse such catalyst particles [3-8]. Alternatively, nanocrystalline Mg alloys can be produced by rapid solidification processes such as melt-spinning [9-17]. With this high-yield rapid cooling technique an amorphous or super-fine microstructure solidifies in the form of ribbons which are a few tens of micrometers thin.

In this contribution, nanocrystalline magnesium-rich Mg-Ni-Y alloys were produced by melt-spinning and were studied in view of their crystal structure, crystallization behaviour and their cyclic hydrogenation/dehydrogenation properties that render them attractive materials for the reversible storage of hydrogen. The alloy composition was chosen for several reasons: From the literature it is known that the addition of Ni to Mg significantly improves the hydriding/dehydriding kinetics and decreases the working temperature compared to that of pure Mg [18-20]. Further, Y is widely known as glass-forming element in Mg alloys [21]. Moreover, ultrafine yttrium hydride particles improve the hydrogen sorption kinetics of Mg [22]. Finally, ultra-fine crystal phases like yttrium hydrides might stabilize the nanostructure of the alloys by preventing further crystal coarsening during thermal processing.

2 Experimental

Mg-Ni-Y master alloys with two different chemical compositions ($\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ and $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$) were produced by induction-melting of a mixture of pure Mg metal, Ni powder and a Ni-Y alloy under Ar atmosphere. During melt-spinning of these alloys, continuous ribbons (35 μm in thickness, 10 mm in width) were obtained from a single roller melt-spinning device (surface

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velocity of 40 m/s). The melt-spinning experiments were carried out under Ar atmosphere. The melt-spun ribbons were thermally activated during three cycles at 350°C and hydrogen partial pressures between 2 and 30 bar for 11 h. This activation procedure is widely found in the literature (cf. Refs. [11, 12, 19]). The crystal structure characterization of the samples has been performed by X-ray diffraction analysis (XRD). The microstructure characterization of the specimens has been carried out using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The hydrogenation/dehydrogenation properties (reaction kinetics) and cycle stability of the melt-spun Mg-Ni-Y ribbons were studied using a magnetic suspension balance.

3 Results and Discussion

XRD patterns of the as-spun $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ and $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$ ribbons are shown in Figure 1. It can be seen that the as-quenched $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$ ribbon shows a typical amorphous structure. $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ ribbons consist of Mg-crystals embedded in an amorphous Mg-Ni-Y phase (002)-peak at 40° (2 Θ). According to TEM, the Mg-Ni-Y alloys produced here consisted in the as-spun state indeed of mixtures of nanocrystalline grains that are embedded in an amorphous matrix (cf. Figure 2).

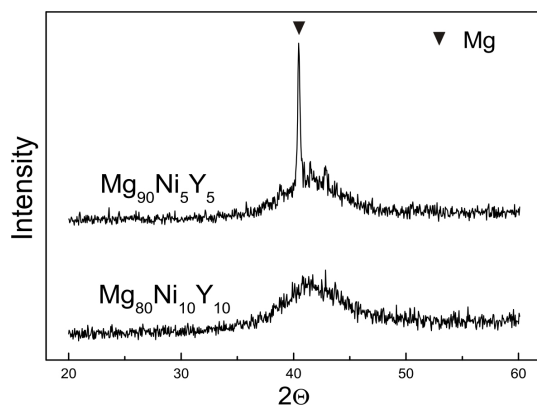


Figure 1: X-ray diffraction patterns for $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ and $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$ in the as-spun state.

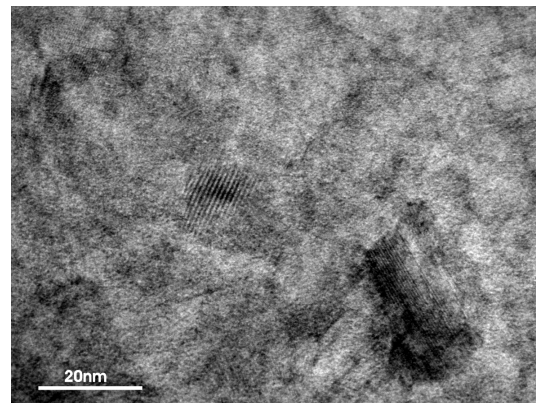


Figure 2: High resolution TEM micrograph of as-spun $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$.

The average crystal size was about 20 nm in the case of $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ (cf. Figure 2) and about 5 nm in the case of $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$ (TEM results not shown). The crystallization temperatures of the as-spun Mg-Ni-Y ribbons were determined by DSC which displayed two and three exothermic peaks for $\text{Mg}_{90}\text{Ni}_5\text{Y}_5$ and $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$, respectively [13]. The characterization of the hydrogenation and dehydrogenation properties of activated Mg-Ni-Y alloys was carried out at different temperatures between 280°C and 180°C. Figure 3 shows the hydrogen content vs. time (reaction kinetics) of the activated $\text{Mg}_{80}\text{Ni}_{10}\text{Y}_{10}$ alloy for the absorption of hydrogen at 20 bar H_2 and the desorption of hydrogen at vacuum. Obviously, the velocity of hydrogenation is nearly equal (approx. 1 wt.-%-H per minute) in the first minutes of hydrogenation during which about 5 wt.-%-H can be achieved. After 4 hours of hydrogenation a saturation of 5.3 wt.-%-H was observed [13]. In the case of dehydrogenation (cf. Figure 3),

there is a clear dependence on the sample temperature in the temperature range investigated. At 280°C and 250°C a 90% desorption is obtained after 5 minutes, at 200°C after 15 min and in the case of 180°C after about 60 minutes. This result of dehydrogenation kinetics is still good enough for automotive application where full desorption needs to be reached after 4 to 5 hours under continuous operation conditions. Thus, it can be expected that $Mg_{80}Ni_{10}Y_{10}$ can be desorbed even at lower temperatures of about 150°C to 160°C which is the operation temperature range of most high-temperature PEM fuel cells [23], thus, waste heat from the fuel cell could be directly used the dehydrogenate the hydride in the tank.

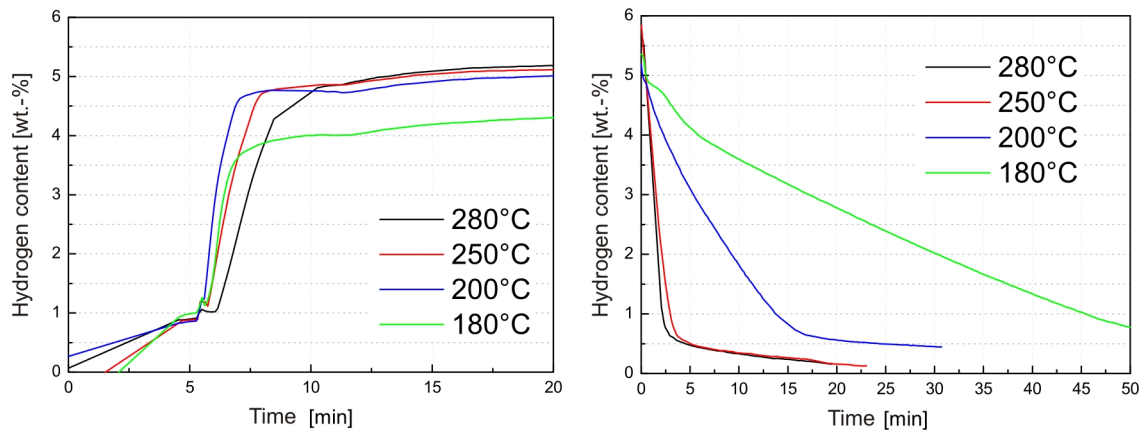


Figure 3: Hydrogenation (left, 20 bar) and dehydrogenation (right, vacuum) kinetics of melt-spun $Mg_{80}Ni_{10}Y_{10}$, measured in a magnetic suspension balance.

From the reaction kinetics point of view, Y is known to form very stable hydrides which act like Mg-Ni hydride phases as catalysts for the hydrogenation of magnesium [22, 24]. Moreover, finely dispersed Y hydride phases might be beneficial regarding the conservation of a sub-micrometer structure of the alloy.

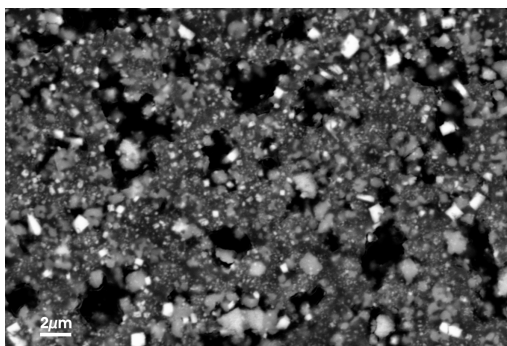


Figure 4: Scanning electron micrograph (SEM) of a hydrogenated $Mg_{80}Ni_{10}Y_{10}$ ribbon after 10.5 hydrogenation/ dehydrogenation cycles.

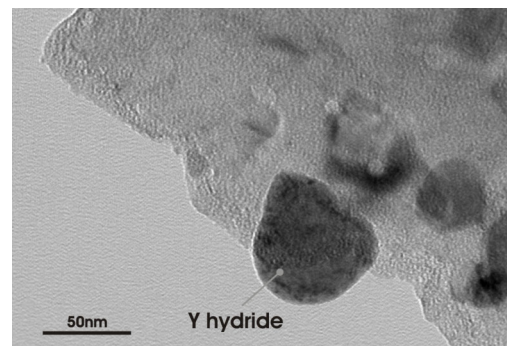


Figure 5: High resolution TEM micrograph of hydrogenated $Mg_{80}Ni_{10}Y_{10}$ after 10.5 hydrogenation/ dehydrogenation cycles.

In this regard, in Figure 4 a SEM micrograph of a hydrogenated $Mg_{80}Ni_{10}Y_{10}$ ribbon after 10.5 hydrogenation/dehydrogenation cycles is shown. Evidently, the material preserves mainly a

sub-micrometer crystal structure which in return might be the case for a fast reaction kinetics during hydrogenation/dehydrogenation.

The cyclically hydrogenated Mg-Ni-Y ribbons were very brittle and could be powderized easily. As shown in Figure 4, the microstructure of ribbons in the hydrogenated state consisted mainly of coarse Mg_2NiH_4 grains with 1 to 2 μm in size and of nanocrystalline yttrium hydride particles embedded in a MgH_2 matrix whose average crystal size is in the range of 100 nm (cf. Figure 5). In the literature, there are only a few investigations on the hydrogenation kinetics of magnesium-rich Mg-Ni-Y alloys. For example, Spassov *et al.* [9, 10] reported results of hydrogen storage properties of the various nanocrystalline and amorphous Mg-Ni-Y alloys ($\text{Mg}_{87}\text{Ni}_{12}\text{Y}_1$, $\text{Mg}_{63}\text{Ni}_{30}\text{Y}_7$, $\text{Mg}_{76}\text{Ni}_{19}\text{Y}_5$, $\text{Mg}_{78}\text{Ni}_{18}\text{Y}_4$, $\text{Mg}_{83}\text{Ni}_{9.5}\text{Y}_{7.5}$) produced by rapid solidification. They found that these Mg-Ni-Y alloys show rather slow rate of hydrogen absorption (0.15 to 0.3 wt.%-H per minute) and a maximum gravimetric hydrogen capacity of about 3.2 wt.%-H. In Ref. [23] the hydrogen sorption properties of Mg-20 wt.% Ni-Y composites prepared by reactive mechanical alloying were studied after the total milling time of 40 h. This composite does not need activation for hydrogen storage process and it can absorb 5.59 wt.%-H at pressures of 30 bar H_2 at 200°C in 10 min and desorb 4.67 wt.%-H at 250°C in 30 min at a hydrogen pressure of 0.2 bar. Compared to these values, the Mg-Ni-Y alloys investigated in this study exhibit even higher hydrogen storage capacities and/or faster hydrogenation/dehydrogenation kinetics. Nonetheless, there is still a need for decreasing the temperatures of hydrogen desorption down to the range of 120°C to 150°C which could be achieved by catalytically more active elements, for example. In conclusion, it could be shown that the melt-spinning technique is very effective in producing nanocrystalline magnesium-rich and catalytically activated alloys, in particular Mg-Ni-Y, which are suitable for the reversible solid-state storage of hydrogen.

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