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Experiment Report Form

ESRF	**Experiment title:** In-situ time-resolved diffraction of phase formation during annealing of amorphous and hydrogenated Mg-Ni-Y alloys	**Experiment number**: MA – 896
Beamline: BM20	**Date of experiment**: from: 18.09.2010 to: 22.09.2010	**Date of report**: 03.03.2010 *Received at ESRF:*
Shifts: **9**	**Local contact(s)**: Dr. Carsten Bähtz (carsten.baehtz@esrf.fr)	

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Report:

The main part of the results reviewed in the present report has been already published in the Journal of Alloys and Compounds [1]. During the experiments at BM20 two rapid solidificated magnesium-rich alloys ($Mg_{90}Ni_{10}$ and $Mg_{80}Ni_{10}Y_{10}$) were investigated. As it was shown recently [2] this systems are very suitable for the reversible solid-state storage of hydrogen, but detailed understanding of recrystallization of amorphous phase as well as of sorption mechanisms is needed. For this reason the main focus of investigations at BM20 was set on the recrystallization behavior of the melt-spun alloys and on the study of the desorption properties of hydrogenated alloys using in-situ synchrotron X-ray diffraction. The incident X-ray beam with an X-ray wavelength of 1.05Å was used for investigation in the scanning range of the diffraction angle between 10° and 35° (2Θ) in reflection geometry.

Recrystallization behavior of melt-spun amorphous Mg-Ni and Mg-Ni-Y

The recrystallization behavior of melt-spun amorphous Mg-Ni and Mg-Ni-Y was studied under different atmospheres (Ar, H_2 and vacuum). The SR-XRD results were compared with the corresponding results obtained by DSC measurement (Fig. 1). Fig 2. shows the evolution of the in-situ SR-XRD of melt-spun Mg-Ni at different temperatures under argon atmosphere. The recrystallization of the amorphous structure starts with nucleation and growth of Mg grains at 125°C. The metastable cubic Mg_6Ni Phase already occurs at 125°C and is decomposed at TA > 200°C into Mg and Mg_2Ni [3,4]. For this system the effect of the different atmospheres was not significant. The result of recrystallization behavior of melt-spun Mg-Ni-Y is more complicated and will be published later.

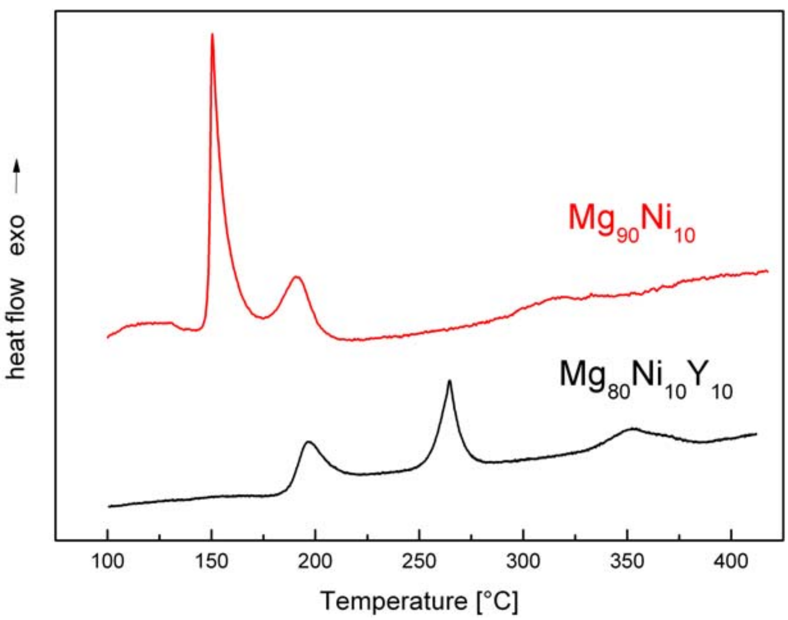

Fig. 1 DSC curves of melt-spun $Mg_{90}Ni_{10}$ and $Mg_{80}Ni_{10}Y_{10}$ (5 K/min, argon).

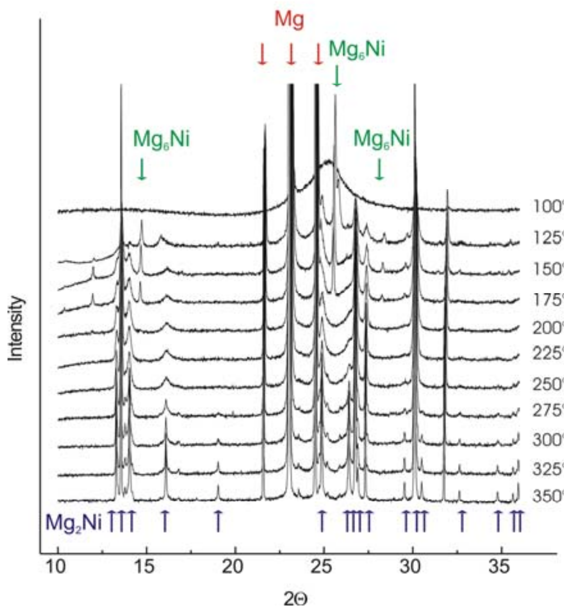

Fig. 2 Evolution of the in-situ SR-XRD pattern of the as spun $Mg_{90}Ni_{10}$

Heat treatment of hydrogenated Mg-Ni and Mg-Ni-Y ribbons under vacuum in the Be-dome annealing chamber

Fig. 3 shows the evolution of the in-situ SR-XRD pattern of the as spun and hydrogenated $Mg_{90}Ni_{10}$ during its vacuum thermal decomposition at 200°C. The X-ray diffraction pattern at *t*=0 min represents the X-ray diffraction pattern of hydrogenated $Mg_{90}Ni_{10}$ at ambient temperature. The heating to 200°C was carried out within the first 4 minutes. During the dehydrogenation of $Mg_{90}Ni_{10}$ two separate processes were identified: desorption of Mg_2NiH_4 to $Mg_2NiH_{0.3}$ and desorption of MgH_2 in the presence of $Mg_2NiH_{0.3}$. The reaction rates are rather different: the dehydrogenation rates for High-Temperature- and Low-Temperature-Mg_2NiH_4 at 200°C in vacuum (10^{-2} mbar) are in the range of 0.2 wt.% H_2/min while for MgH_2 it could be calculated as 0.1 wt.% H_2/min [1]. The improved kinetics of hydrogen desorption for Mg-Ni can be explained by the presence of $Mg_2NiH_{0.3}$ as the active catalyst phase. Unexpectedly, in-situ SR-XRD investigations of the thermal decomposition of $Mg_{80}Ni_{10}Y_{10}$ revealed that no formation of $Mg_2NiH_{0.3}$ is observed in this case during the dehydrogenation (Fig. 4). The reason for this behaviour may be explained by the fact that yttrium can be solved in Mg_2Ni causing a lattice parameter expansion. For more detailed results, including the results of Rietveld analysis (phase abundance and lattice parameters) and TGA results please see [1].

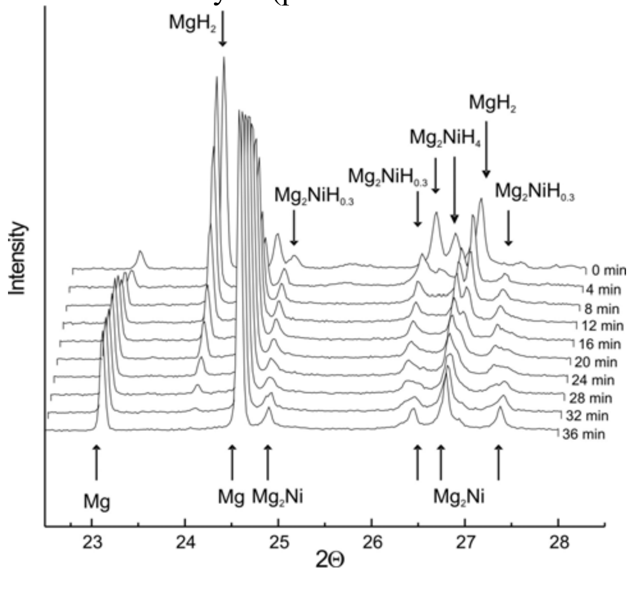

Fig. 3: Evolution of the in-situ SR-XRD pattern of the as spun and hydrogenated $Mg_{90}Ni_{10}$ during its vacuum thermal decomposition at 200°C (pressure: 10^{-2} mbar).

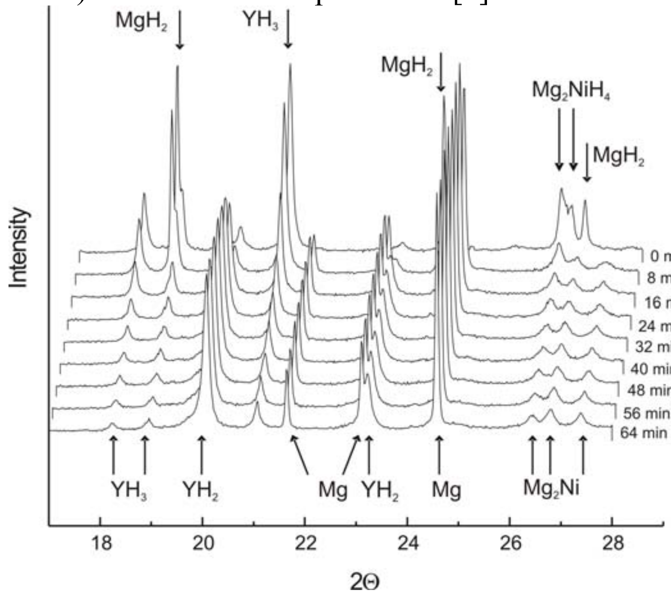

Fig. 4: Evolution of the in-situ SR-XRD pattern of hydrogenated $Mg_{80}Ni_{10}Y_{10}$ during its vacuum thermal decomposition at 200°C (pressure: 10^{-2} mbar).

Conclusion

In order to understand the phase transformations and the dehydrogenation reactions of the melt-spun Mg-Ni(-Y), the recrystallization and desorption properties were studied by in-situ synchrotron X-ray diffraction performed at the Rossendorf Beamline (BM20) of the ESRF.
Primarily, the results of desorption mechanisms of hydrogenated Mg-Ni and Mg-Ni-Y reveal interesting differences in the investigated systems (Fig. 3 and 4). It was found that the kinetics of H-desorption is controlled by the two-step hydrogen desorption process in case of Mg-Ni. In the case of $Mg_{80}Ni_{10}Y_{10}$ no formation of the $Mg_2NiH_{0.3}$ phase was observed
The results of these investigations have been published in the Journal of Alloys and Compounds [1].

Acknowledgement

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References

[1] S. Kalinichenka, L. Rontzsch, C. Baehtz, B. Kieback, Hydrogen desorption kinetics of melt-spun and hydrogenated $Mg_{90}Ni_{10}$ and $Mg_{80}Ni_{10}Y_{10}$ using in-situ synchrotron, X-ray diffraction and thermogravimetry, *J Alloys Comp*, In Press, Accepted Manuscript, Available online 24 February 2010, ISSN 0925-8388, DOI: 10.1016/j.jallcom.2010.02.128 .

[2] S. Kalinichenka, L. Röntzsch, B. Kieback, Structural and hydrogen storage properties of melt-spun Mg–Ni–Y alloys, Intl. J. Hydrogen Energy 34 (2009) 7749.

[3] T. Spassov, St. Todorova, V. Petkov, Kinetics of Mg6Ni nanocrystallization in amorphous Mg83Ni17, Journal of Non-Crystalline Solids, Volume 355, Issue 1, 1 (2009) 1

[4] A. Teresiak, M. Uhlemann, J. Thomas, A. Gebert, The metastable Mg~6Ni phase—Thermal behaviour, crystal structure and hydrogen reactivity of the rapidly quenched alloy, *J Alloys Comp*, Volume 475, Issues 1-2, 5 (2009) 191.