ROBL-CRG	**Experiment title:** In-situ synchrotron X-ray diffraction studies of the crystallization and hydrogen sorption properties of rapidly quenched Mg-Ni-Y-(Cu) alloys	**Experiment number**: **20-02-694**
Beamline: BM 20	**Date of experiment**: from: 6.4.2010-13.4.2010	**Date of report**: 01.09.2010
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Names and affiliations of applicants (* indicates experimentalists):

Lars Röntzsch*[1)], Siarhei Kalinichenka[*2)]

1) Fraunhofer Institute for Manufacturing Technology and Applied Materials Research, Winterbergstraße 28, 01277 Dresden, Germany
2) Institute for Materials Science, Dresden University of Technology, Helmholtzstraße 7, 01069 Dresden, Germany

Results

The Mg-Cu-Ni-Y alloys exhibit good hydrogen storage properties which makes these materials especially attractive for solid-state hydrogen [1]. However, the phase transformation during crystallization and hydrogen (de)sorption of Mg-based alloys have remained largely undetermined experimentally.
The aim of the in-situ diffraction study at the Rossendorf beamline ESRF-BM20 was to investiagte the crystal phase formation processes during thermal annealing of the amorphous as-spun Mg-Cu-Ni-Y alloys, and furthermore, the desorption of hydrogeneted ribbons under vacuum.

Recrystallization behavior

The recrystallization behavior of melt-spun amorphous Mg-Ni-Cu-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 $Mg_{85}Cu_5Ni_5Y_5$ at different temperatures under argon atmosphere (for this system the effect of the different atmospheres was not significant). The incident X-ray beam with an X-ray wavelength of 1.05 Å was used for this investigations.
The crystallization of the amorphous structure starts with nucleation and growth of Mg and Mg_2Cu grains at 150°C. The XRD data also shows that at 200°C the formation of MgY occurs. The final composition of the sample at 250° is Mg, MgY and Mg_2Cu. It is interesting that no metallic Ni or Ni-phases diffraction peaks can be observed. The reason for this finding could be explained by forming of Ni-substituted Mg_2Cu [2].
The results of recrystallization behavior of melt-spun Mg-Ni-Y provide imortant information regarding the activation of as-spun ribbons.

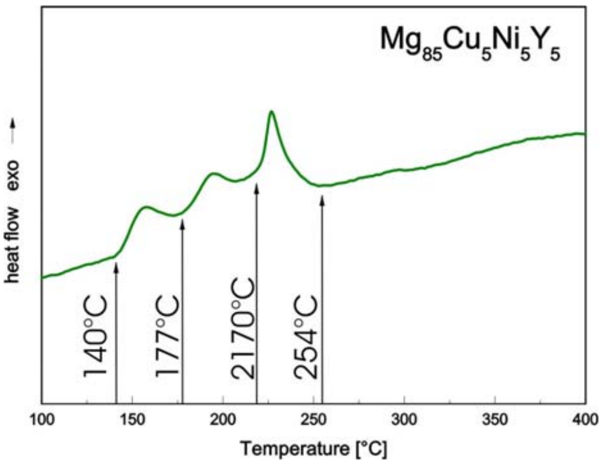


Fig. 1: DSC curve of melt-spun $Mg_{85}Cu_5Ni_5Y_5$ (5 K/min, Ar).

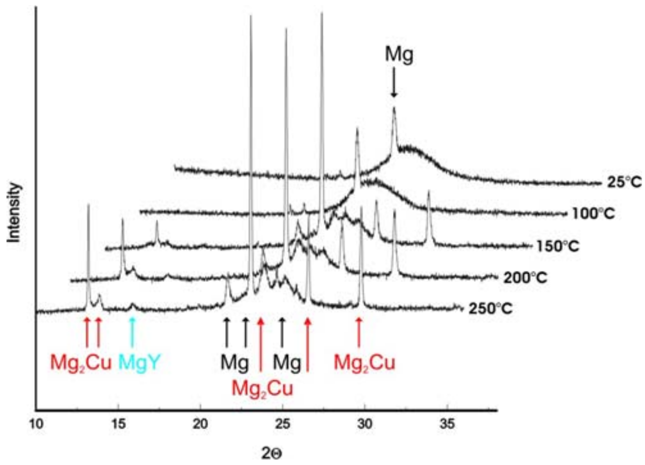


Fig. 2: Evolution of the in-situ SR-XRD pattern of the as spun $Mg_{85}Cu_5Ni_5Y_5$.

Heat treatment of hydrogenated Mg-Cu-Ni-Y ribbon under vacuum in the stainless steel dome designed with Kapton windows.

The evolution of the in situ SR-XRD patterns of the as-spun and hydrogenated $Mg_{85}Cu_5Ni_5Y_5$ during vacuum thermal decomposition at 200 °C (10^{-2} mbar) is presented in Fig. 3. The X-ray diffraction pattern at t=0 min represents the X-ray diffraction pattern of hydrogenated samples at ambient temperature.

During the dehydrogenation of $Mg_{85}Cu_5Ni_5Y_5$ several processes can be identified: decomposition of the hydride phases according to Eqns. (1) to (4) and transformation of $MgCu_2$ to Mg_2Cu according to Eq. 5. It must be noted, that these dehydrogenation reactions take place simultaneously.

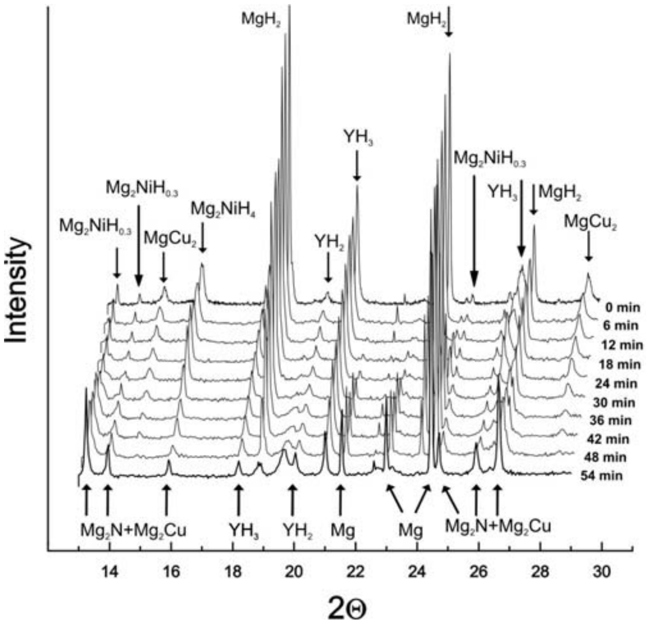
$$MgH_2 \longrightarrow Mg + H_2 \quad (1)$$

$$Mg_2NiH_4 \longrightarrow Mg_2Ni + 2\,H_2 \quad (2)$$

$$Mg_2NiH_{0.3} \longrightarrow Mg_2Ni + 0.15\,H_2 \quad (3)$$

$$2\,YH_3 \longrightarrow 2\,YH_2 + H_2 \quad (4)$$

$$2\,Mg_2Cu + 3H_2 \longrightarrow 3\,MgH_2 + MgCu_2 \quad (5)$$



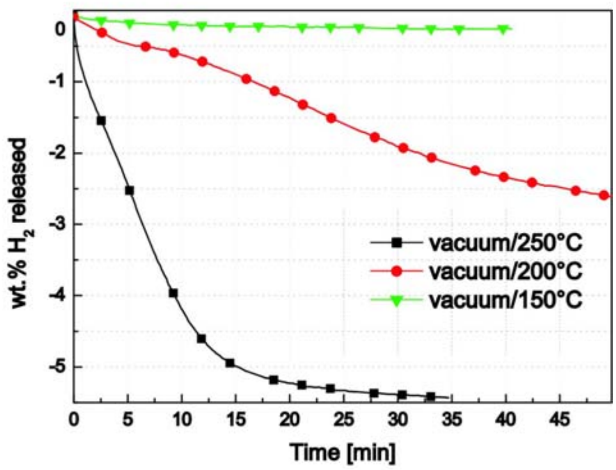


Fig. 3. The evolution of the in situ synchrotron XRD pattern of melt-spun and hydrogenated $Mg_{85}Cu_5Ni_5Y_5$ during its isothermal dehydrogenation at 200°C and at a pressure of 10^{-2} mbar H_2.

After dehydrogenation five phases have been observed in the material: Mg, Mg_2Ni, Mg_2Cu, YH_2 and YH_3. These XRD results of the dehydrogenated sample are similar to literature data, e.g. for $Mg_{60}Ni_{10}Cu_{30}$ prepared by ball milling [3]. It is also evident that the transformation of YH_3 into YH_2 is the slowest step of the reaction and even after 54 minutes at 200°C a residual amount of YH_3 can be observed in the diffraction pattern.

Conclusion

In order to understand the crystallization behavior and the dehydrogenation reactions of the melt-spun Mg-Cu-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.

Particularly, the results of desorption mechanisms of hydrogenated $Mg_{85}Cu_5Ni_5Y_5$ reveal interesting differences between Mg-Cu-Ni-Y alloy and the recently investigated systems [4, 5]. The SR-XRD results indicated that the dehydrogenation of the hydride phases and the transformation of $MgCu_2$ to Mg_2Cu take place at the same time and no formarion of hydrogen transfer phase was observed.

The results of these investigations have been already presented at International Symposium on Metal-Hydrogen Systems 2010 and submitted for publishing in the Journal of Alloys and Compounds [1].

References

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