Mössbauer study of Mg-Ni(Fe) alloys processed as materials for solid state hydrogen storage

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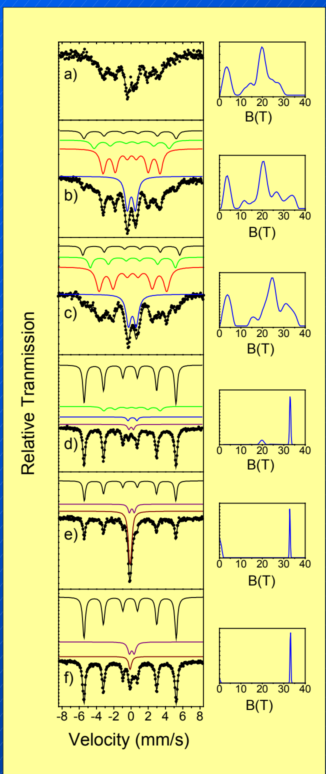
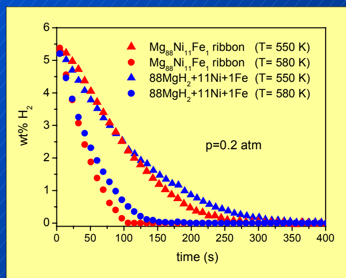
Magnesium-rich Mg-Ni-Fe intermetallics have been prepared by two different routes:

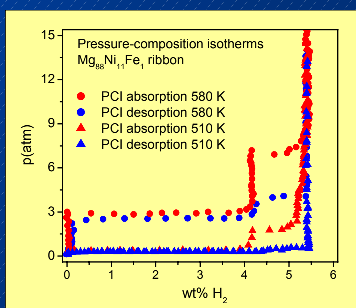
1) short time ball milling of $Mg_{88}Ni_{11}Fe_1$ ribbons obtained by melt-spinning
2) long time ball milling of a mixture of MgH_2, Ni and Fe powders with similar composition

MATERIALS CHARACTERISATIONS (XRD, Mössbauer spectroscopy, hydrogen absorption/desorption, pressure composition isotherms)





milled ribbons exhibit better desorption kinetics than milled powder mixture



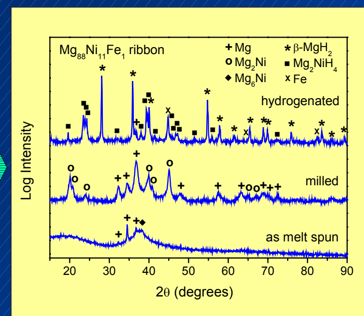
ribbons

As melt spun ribbons are mainly amorphous

The main phases formed during milling are Mg and Mg_2Ni

β-MgH_2 and Mg_2NiH_4 are mainly present after hydrogenation

Iron can be detected from XRD patterns in the hydrogenated sample only as α-Fe

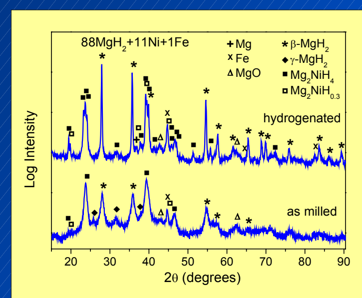


milled powders mixture

Milled powders mixture contains mainly β-MgH_2 and Mg_2NiH_4.

After hydrogenation the same phases are present, but with higher crystalline size

Iron can be detected in XRD patterns before and after hydrogenation only as α-Fe



Pressure-composition isotherms in absorption and desorption mode exhibit a double plateau behaviour corresponding to β-MgH_2 (lower plateau), and Mg_2NiH_4 (upper plateau).

Thermodynamics of β-MgH_2 and Mg_2NiH_4 formation/dissociation is not changed with respect pure phases.

Fitted Mössbauer hyperfine parameters of analysed samples

Sample	Phase	δ (mm/s)	Δ (mm/s)	B_{hf} (T)	Rel. Area (%)
$Mg_{88}Ni_{11}Fe_1$ milled ribbon (293 K)	α-Fe	0.03(2)	0.06(5)	33.2(2)	12(2)
	Fe-Ni(Mg)	0.18(1)	0.02(1)	20.5(1)	47(1)
	$FeNi_3$ (Mg)	0.21(3)	0.04(4)	27.0(3)	16(2)
	Mg_2Ni(Fe)	0.15(1)	0.94(2)	-	25(1)
$Mg_{88}Ni_{11}Fe_1$ milled ribbon (80 K)	α-Fe	0.09(3)	0.09(6)	34.5(4)	11(3)
	Fe-Ni(Mg)	0.31(3)	0.03(2)	24.3(2)	50(3)
	$FeNi_3$ (Mg)	0.33(3)	0.02(5)	30.6(4)	15(3)
	Mg_2Ni(Fe)	0.26(2)	0.89(3)	-	24(2)
$Mg_{88}Ni_{11}Fe_1$ ribbon hydrog.	α-Fe	0.002(2)	0.002(2)	33.03(2)	76(1)
	Fe-Ni(Mg)	0.19(3)	0.06(5)	20.3(3)	15(1)
	Mg_2Ni(Fe)	0.28(3)	1.03(6)	-	4(1)
	Fe^{3+} oxide	0.13(3)	0.53(5)	-	5(1)
$88MgH_2$ + 11Ni + 1Fe as milled	α-Fe	0.005(4)	0.005(5)	32.95(4)	46(2)
	Fe (SP)	0.00(1)	0.2(1)	-	43(3)
	Fe^{3+} oxide	0.20(5)	0.6(2)	-	11(4)
$88MgH_2$ + 11Ni + 1Fe hydrog.	α-Fe	0.002(2)	0.005(3)	33.16(2)	80(1)
	Fe (SP)	0.00(4)	0.0(3)	-	7(3)
	Fe^{3+} oxide	0.20(3)	0.56(4)	-	13(3)

Mössbauer spectra

$Mg_{88}Ni_{11}Fe_1$ ribbon:
a) as melt spun (RT)
b) milled (RT)
c) milled (80 K)
d) milled and hydrogenated (RT)

milled powders mixture:
e) as milled
f) milled and hydrogenated

fitted spectral components:
— Fe-Ni(Mg)
— Fe at Mg_2Ni g b
— metallic Fe
— $FeNi_3$(Mg)
— SPM Fe
— iron oxide impurity

Mössbauer interpretation

- The Mössbauer spectrum of milled ribbon (b) is similar to that of as melt spun ribbon (a), but the linewidth is sharper. This suggests an increase of crystallinity (confirmed by XRD data), but conserving the local environment of most iron atoms almost unchanged
- Spectral components in (b) are: Fe-Ni(Mg) and Fe/Mg_2Ni grain boundaries; small contribution $FeNi_3$(Mg) and α-Fe
- No relaxation effect nor phase transitions are observed in milled ribbon from RT to 80K (b,c)
- Hydrogenated milled ribbon (d): main contribution α-Fe; small contribution Fe-Ni(Mg) and Fe/Mg_2NiH_4 g b; small amount of Fe^{3+} oxide in SPM relaxation state
- Milled powders mixture (e): mainly SPM-Fe/α-Fe (1/1 ratio); small amount of Fe^{3+} SPM oxide
- Hydrogenated milled powders mixture (f): mainly α-Fe, minor SPM-Fe, small amount of Fe^{3+} SPM oxide

CONCLUSIONS

- Mg-Ni-Fe compounds obtained by melt-spinning and subsequently ball milling show better hydrogen desorption kinetics than similar samples obtained by milling a mixture of MgH_2, Ni and Fe commercial powders.
- In milled ribbons a sort of catalytic effect on the gas-solid reaction seems to come from Fe located at Mg_2Ni grain boundaries
- Again in milled ribbons α-Fe separates from Mg-Ni matrix during absorption/desorption cycles leaving unchanged the thermodynamics of hydride formation and dissociation.