CO$_2$ reactivity with Mg$_2$NiH$_4$ synthesized by *in situ* monitoring mechanical milling

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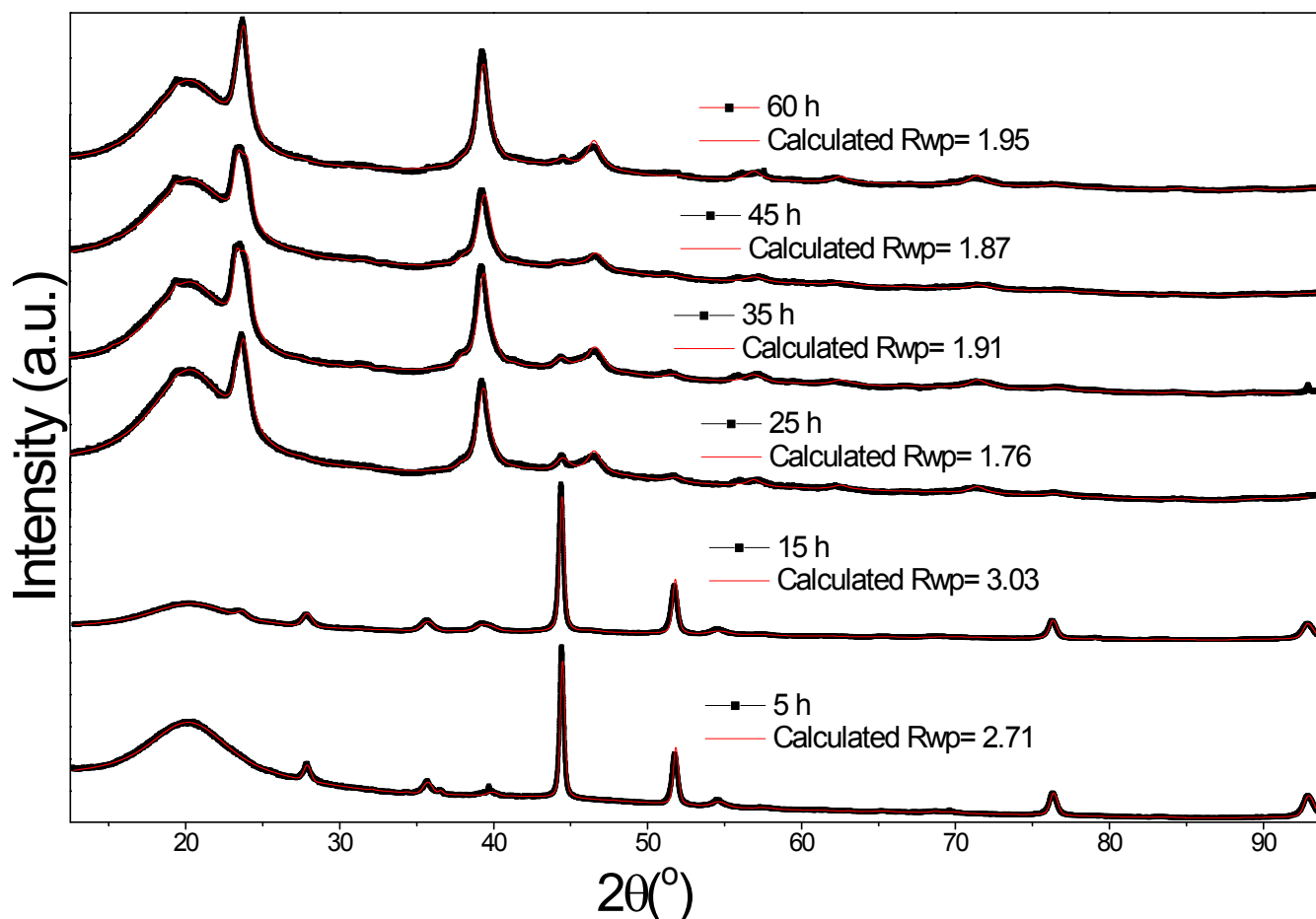
Figure S1 – Diffractograms taken at different milling times and Rietveld fitting for quantitative analyses.

Milling time (h)	Ni	Mg	MgH2	LT - Mg2NiH4 (C2/c1)	HT - Mg2NiH4 (Fm3-m)	Mg2NiH4		Rwp (%)
5	66.4±0.6	3.2±0.10	30.4±0	-	-	0		2.71
15	64.1±0.5	-	26.8±0	-	9.1±0.1	9.1	±0.1	3.03
25	8.6±0.5	-	-	7.5±0.2	83.9±0.9	91.4	±1.0	1.76
35	5.6±0	-	-	20.2±0.6	74.2±1	94.4	±2.0	1.91
45	3.3±0	-	-	29.1±1	67.6±2	96.7	±3.0	1.87
60	3.5±0	-	-	5.7±0.2	90.8±2	96.5	±2.0	1.95

Table S1 – Amounts of phases during the milling process expressed in wt.%. Results coming from Rietveld analyses of samples taken at different milling times (Diffractograms and fittings shown in Figure S2). HT–Mg_2NiH_4 (Cubic, S.G. *Fm*-3*m*) and LT–Mg_2NiH_4 (LT1, Monoclinic, S.G. *C12/c1*).
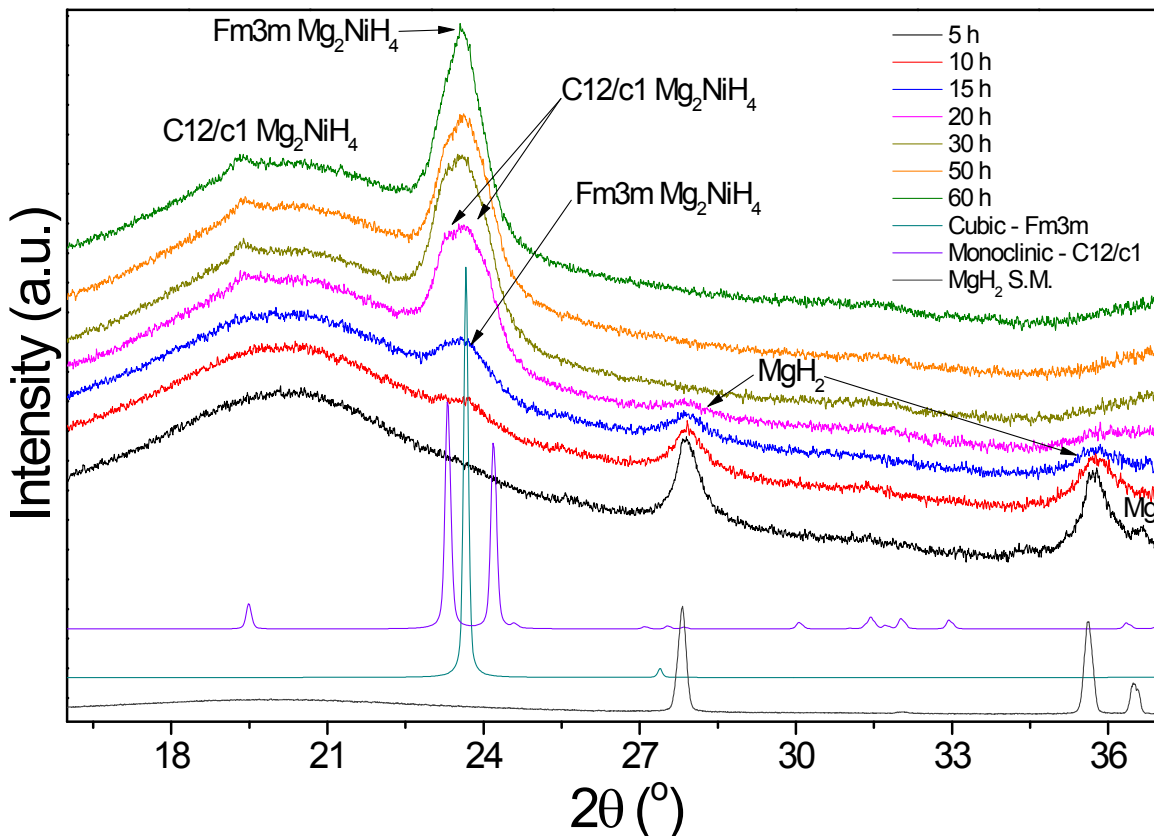
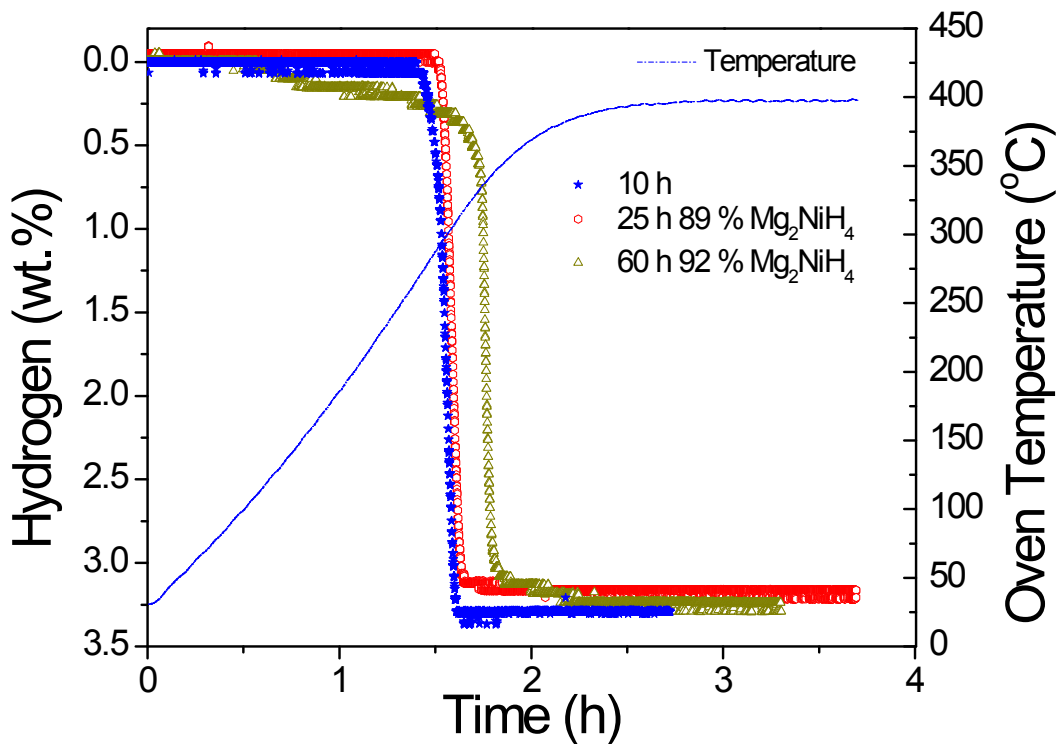**Figure S2 –** Diffractograms taken at different milling times from 15º to 40º.

Figure S3 - Non-isothermal dehydrogenation curves for $2MgH_2$-Ni at 10 h, 25 h and 60 h of mechanical milling. Heating ramp of about 3 ºC/min from 25 ºC to 400 ºC under 1 bar H_2.
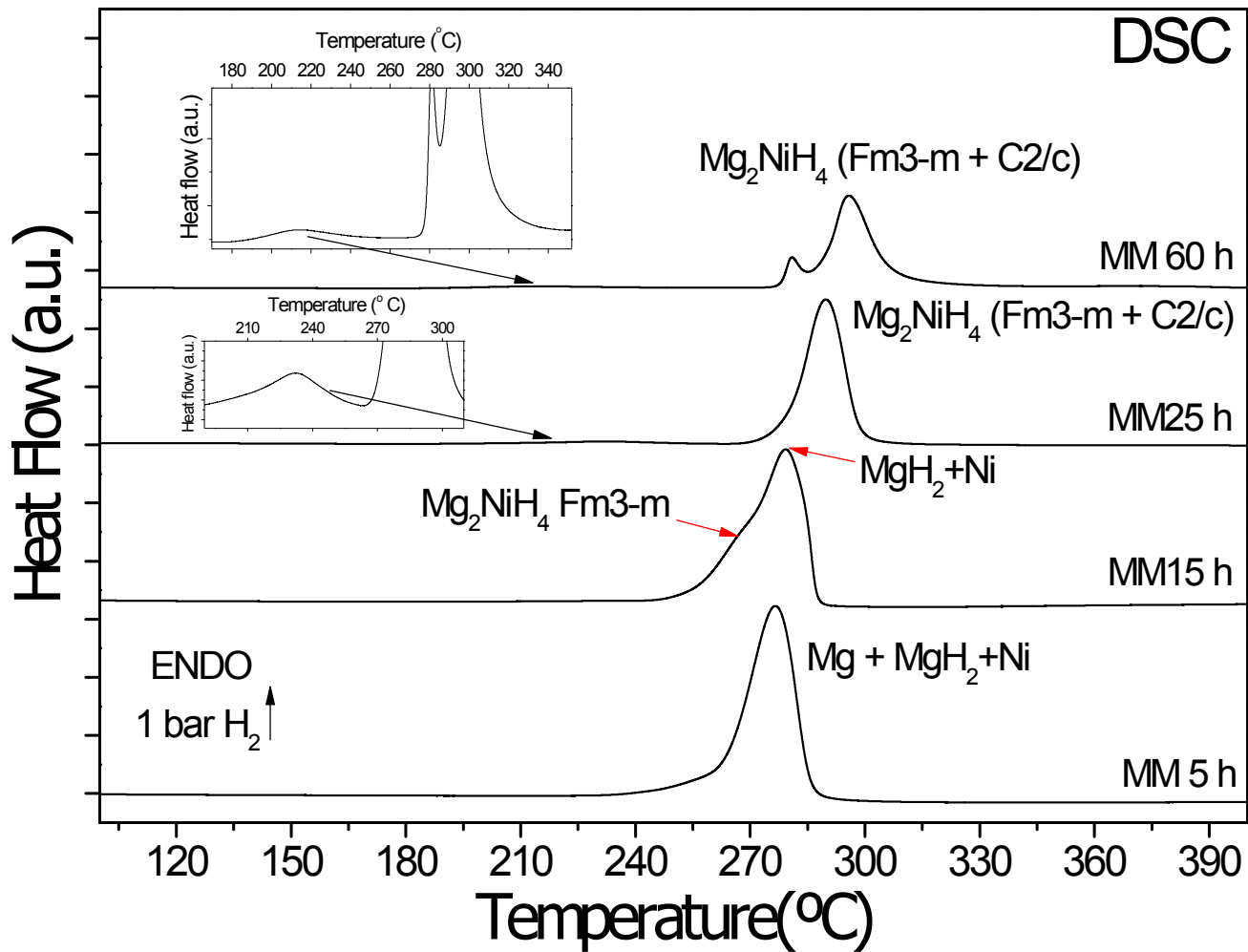
Figure S4 – HP – DSC for $2MgH_2$-Ni material upon milling: 5 h, 15 h, 25 h and 60 h. Heating ramp 5 $^{\circ}$C/min and under 1 bar H_2.

5 h MM

Mean size: 20 μm
Range: 5 - 50 μm

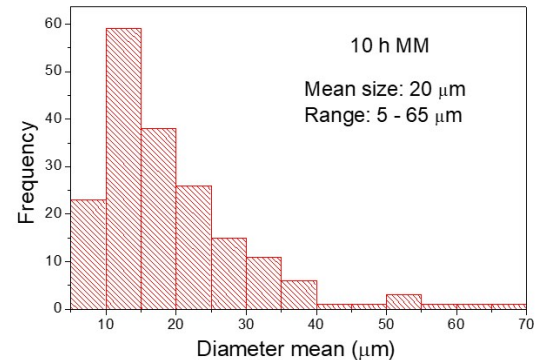10 h MM

Mean size: 20 μm
Range: 5 - 65 μm

20 h MM

Mean size: 15 μm
Range: 5 - 55 μm

30 h MM

Mean size: 10 μm
Range: 3 - 30 μm
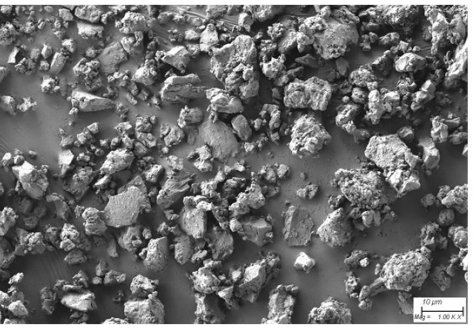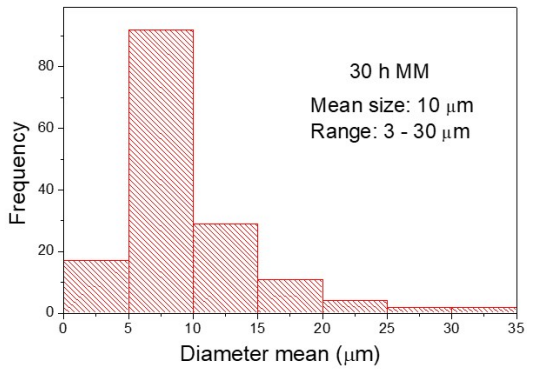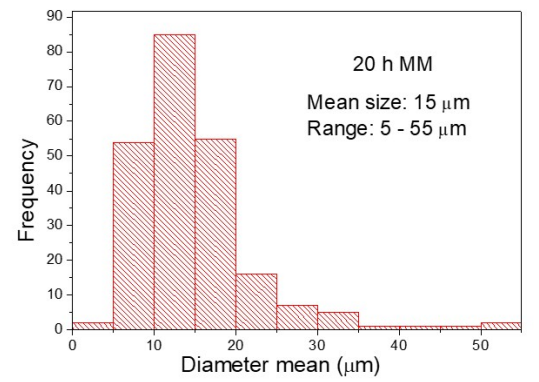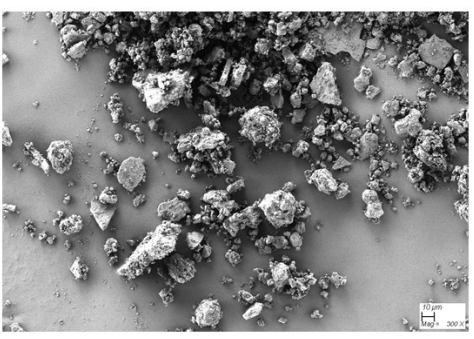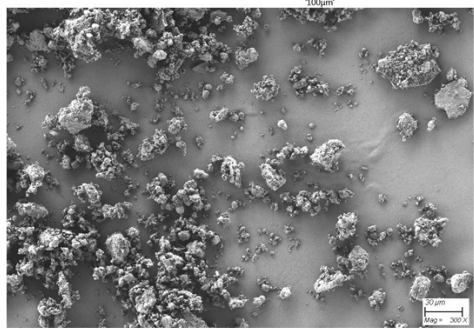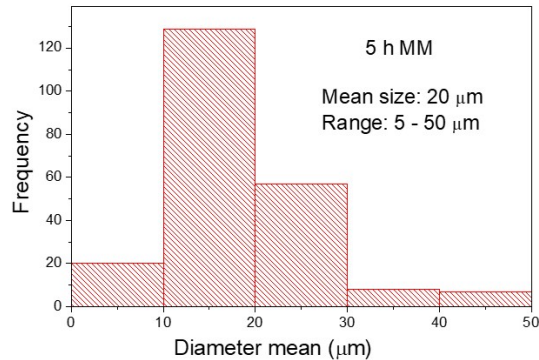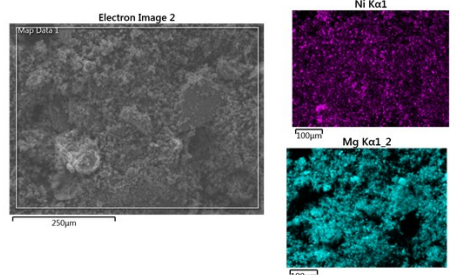
Figure S5 – Particle size distributions (PSDs), Scanning electron microscopy (SEM) observations and mapping.

Figure S6 – Crystallite size evolution during milling for MgH_2, Ni and Mg_2NiH_4.
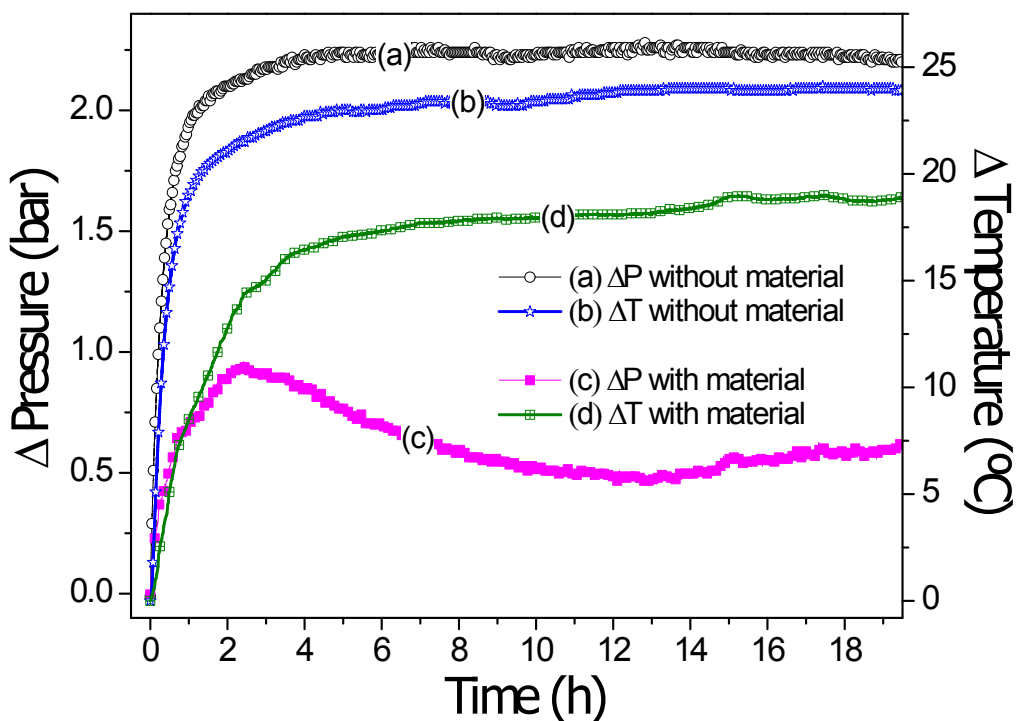
Figure S7 – Comparison between temperature and pressure evolution during the first 20 h of milling with and without material.

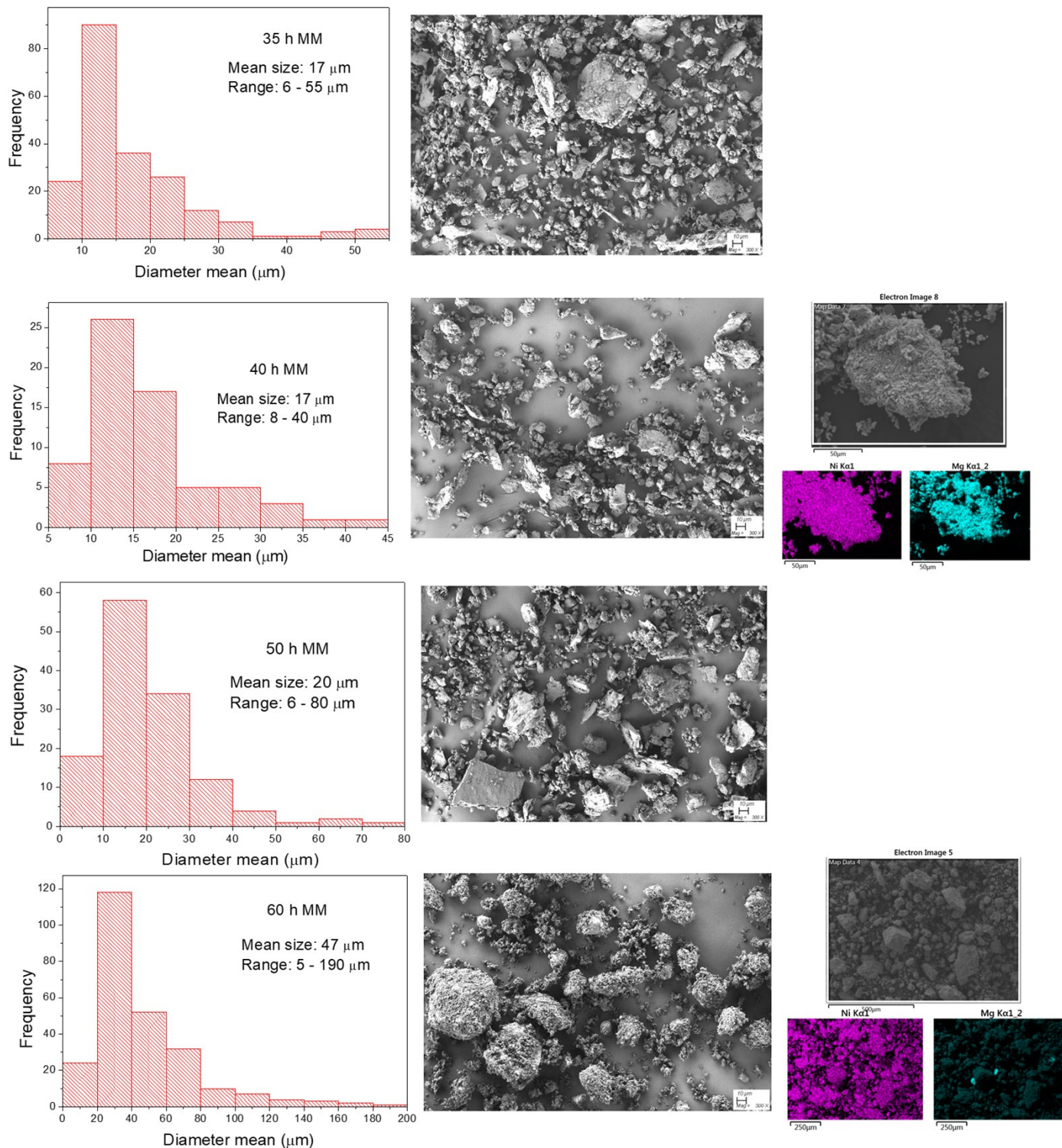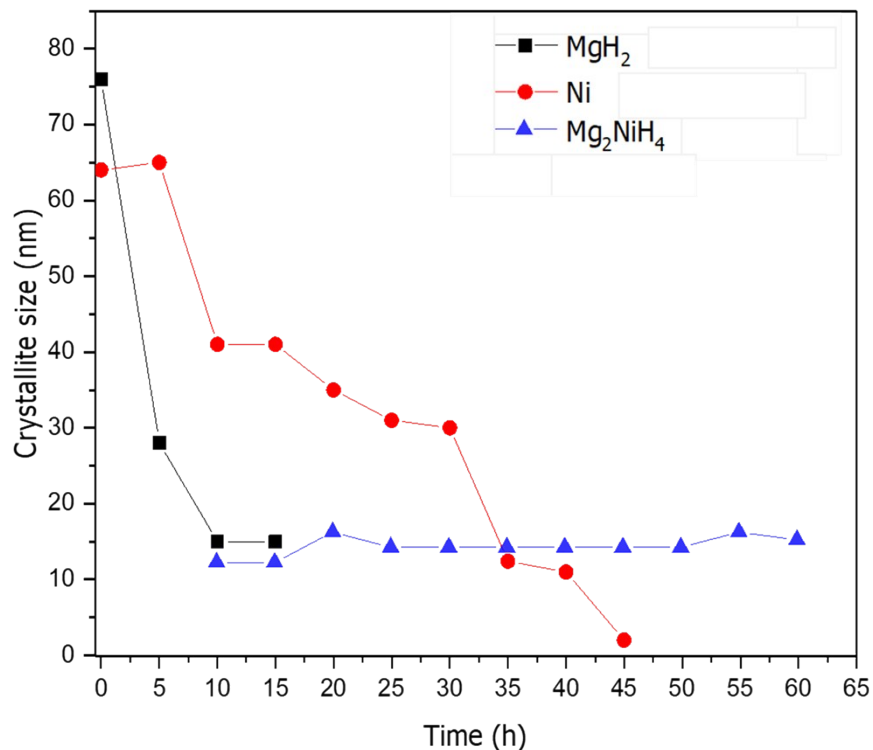**Hydrogen consumption at the beginning of the milling process**

From Fig.S7 – Curves (c) and (d) expressed as were measured (not in delta). From these curves the data of the gas phase is subtracted:
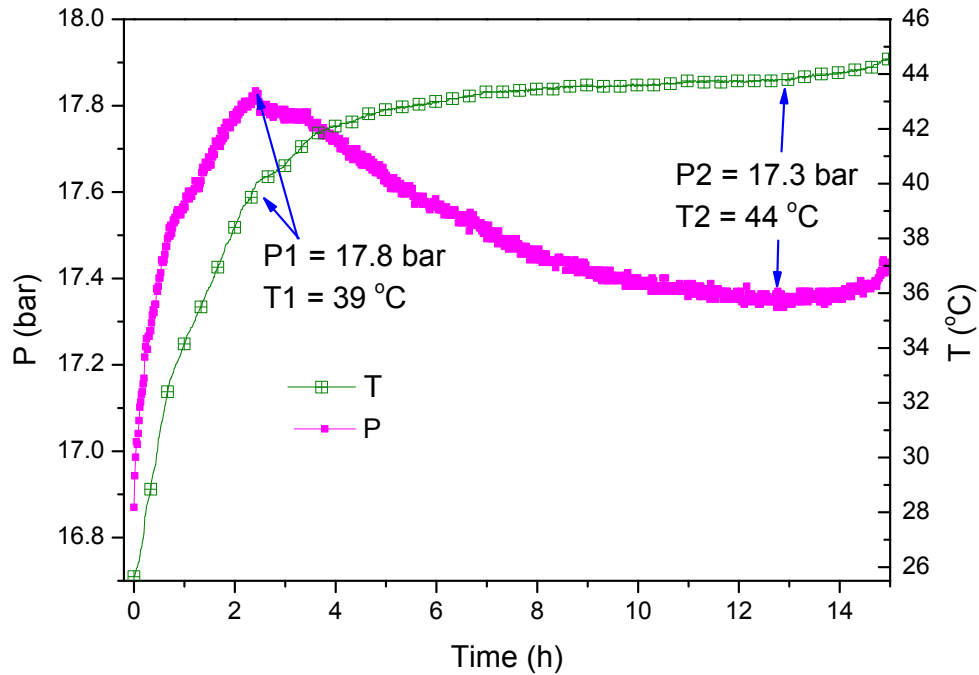
Volume of the milling chamber = 0.2 L

R = 0.082 L.atm/K mol

Ideal gas equation P.V = n.R.T

State 1

n1 = P1.V/R.T1

n1 = (17.5 atm . 0.2 L) / (0.082 L.atm/K mol . 312 K)

n1 = 0.1368 mol

State 2

n2 = P2.V/R.T2

n2 = (17.0 atm . 0.2 L) / (0.082 L.atm/K mol . 317 K)

n2 = 0.1307 mol

Consumed moles Δn = (0.1368 – 0.1307) mol

Δn = 0.0060 mol

It is assumed that the free Mg reacts with H_2 to form MgH_2

$Mg_{(s)} + H_{2(g)} \rightarrow MgH_{2(s)}$
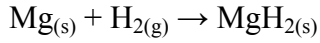
Amount of Mg = 0.0060 mol * 24.31 g/mol

Amount of Mg = 0.146 g

wt.% of free Mg = (0.146 g/5 g sample) * 100

wt.% of free Mg = 2.92

Figure S8 – High-pressure differential scanning calorimetry (HP–DSC) for as-sintered Mg_2NiH_4[16] and as-milled Mg_2NiH_4. Heating ramp 5 °C/min and under 1 bar H_2.

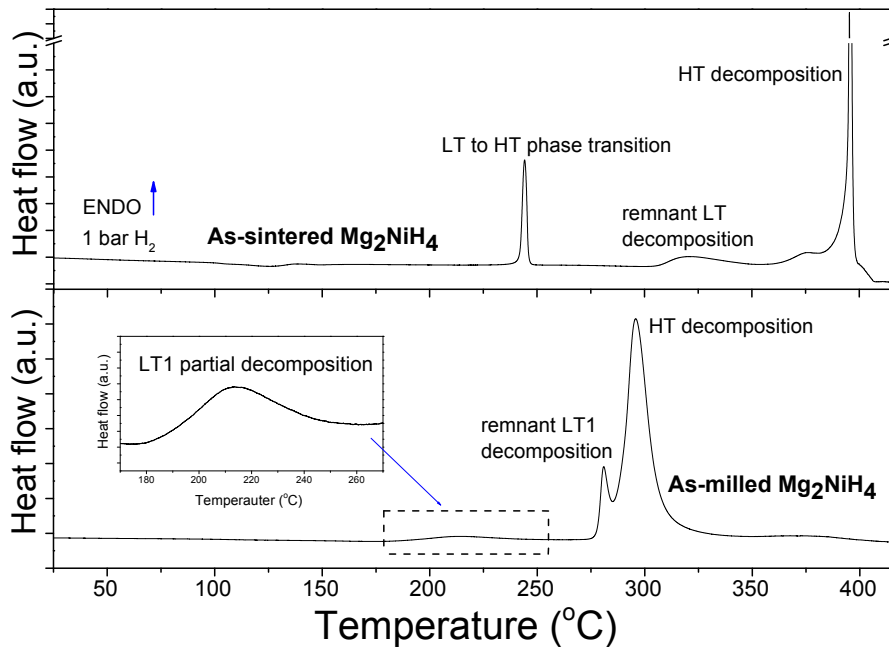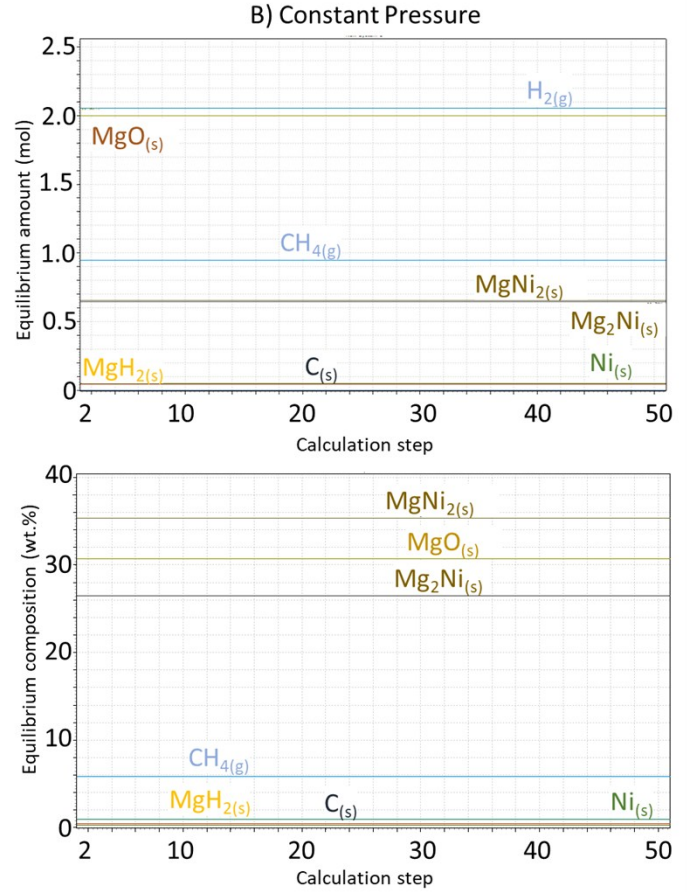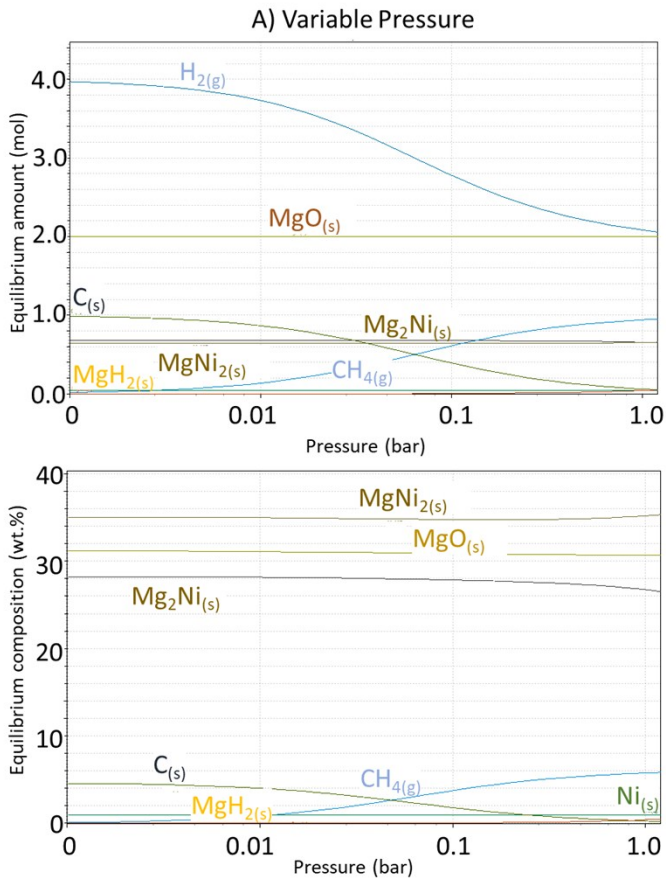| Equilibrium Amount at variable pressure Final temperature and pressure conditions		
Species	Mol	Mol %
$CO_{2(g)}$	0.0	0.0
$H_{2(g)}$	2.05	32.0
$Mg_2Ni_{(s)}$	0.65	10.0
$MgNi_{2(s)}$	0.65	10.0
$O_{2(g)}$	0.000	0.0
$CO_{(g)}$	0.000	0.0
$H_2O_{(g)}$	0.000	0.0
$CH_{4(g)}$	0.95	15.0
$C_2H_{4(g)}$	0.000	0.0
$Ni_{(s)}$	0.04	0.60
$CH_3OH_{(g)}$	0.000	0.0
$C_{(s)}$	0.05	0.70
$MgO_{(s)}$	2.000	31.0
$MgCO_{3(s)}$	0.000	0.0
$NiCO_{3(s)}$	0.000	0.0
$H_2O_{(l)}$	0.000	0.0
$C_2H_{6(g)}$	0.000	0.0
$MgH_{2(s)}$	0.05	0.70

Equilibrium Amount at constant pressure Last step of the calculation		
Species	Mol	Mol %
$CO_{2(g)}$	0.0	0.0
$H_{2(g)}$	2.05	32.0
$Mg_2Ni_{(s)}$	0.649	10.0
$MgNi_{2(s)}$	0.654	10.0
$O_{2(g)}$	0.000	0.0
$CO_{(g)}$	0.000	0.0
$H_2O_{(g)}$	0.000	0.0
$CH_{4(g)}$	0.949	15.0
$C_2H_{4(g)}$	0.000	0.0
$Ni_{(s)}$	0.042	0.60
$CH_3OH_{(g)}$	0.000	0.0
$C_{(s)}$	0.051	0.70
$MgO_{(s)}$	2.000	31.0
$MgCO_{3(s)}$	0.000	0.0
$NiCO_{3(s)}$	0.000	0.0
$H_2O_{(l)}$	0.000	0.0
$C_2H_{6(g)}$	0.000	0.0
$MgH_{2(s)}$	0.05	0.70

Figure S9 – Equilibrium amounts of phases calculated at 400 °C, $4H_2:1CO_2$ stoichiometric ratio and volume of 10 cm³: A – under variable pressure up to 1.2 bar and B –constant pressure of 1.2 bar.

Reaction Equation
2Mg2NiH4(s) + CO2(g) = 0.75Mg2Ni(s) + 2MgO(s) + 0.25Ni(s) + 0.5MgNi2(s) + C(s) + 4H2(g)

Reaction Data

T	ΔH	ΔS	ΔG	K	Log K
°C	kJ	J/K	kJ		
25.000	-535.517	314.791	-629.371	1.873E+110	110.273
50.000	-535.494	314.862	-637.242	1.032E+103	103.014
75.000	-535.395	315.155	-645.116	6.282E+096	96.798
100.000	-535.228	315.617	-653.001	2.610E+091	91.417
125.000	-535.001	316.205	-660.898	5.162E+086	86.713
150.000	-534.719	316.892	-668.812	3.687E+082	82.567
175.000	-534.386	317.657	-676.744	7.678E+078	78.885
200.000	-534.003	318.487	-684.695	3.936E+075	75.595
225.000	-533.574	319.370	-692.668	4.339E+072	72.637
250.000	-533.104	320.290	-700.664	9.219E+069	69.965
275.000	-532.596	321.238	-708.683	3.451E+067	67.538
300.000	-532.049	322.214	-716.726	2.114E+065	65.325
325.000	-531.460	323.219	-724.794	1.993E+063	63.299
350.000	-530.825	324.260	-732.887	2.744E+061	61.438
375.000	-530.146	325.328	-741.007	5.285E+059	59.723
400.000	-529.456	326.373	-749.154	1.372E+058	58.137

Table S2 – Thermodynamic data for the reaction between $2Mg_2NiH_{4(s)} + CO_{2(g)}$ (4).