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Supplementary Materials for

Insights into the composition exploration of novel hydrogen storage alloys: Evaluation of the Mg−Ni−Nd−H phase diagram

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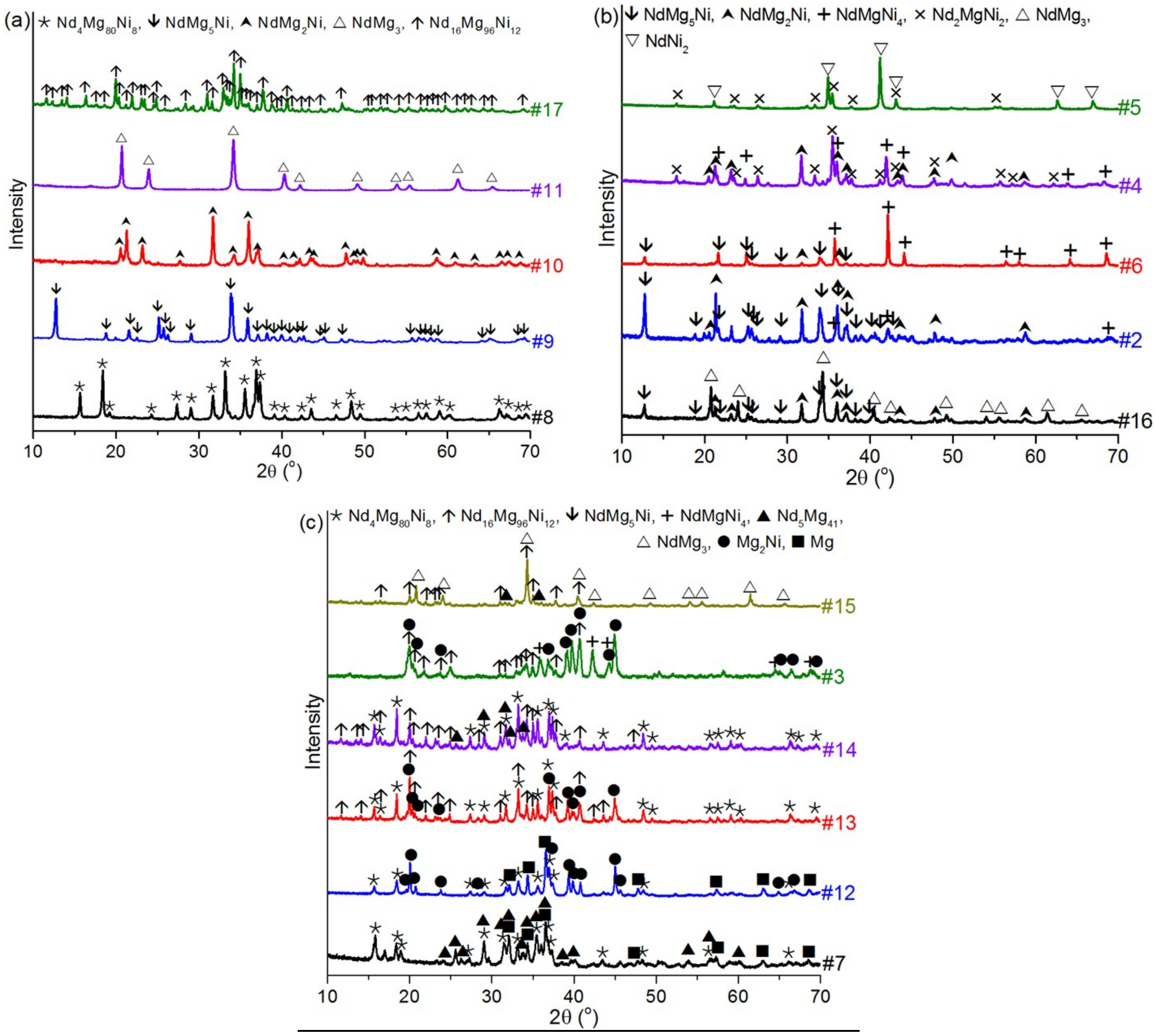

Fig. S1. The XRD patterns of samples annealed at 400 °C

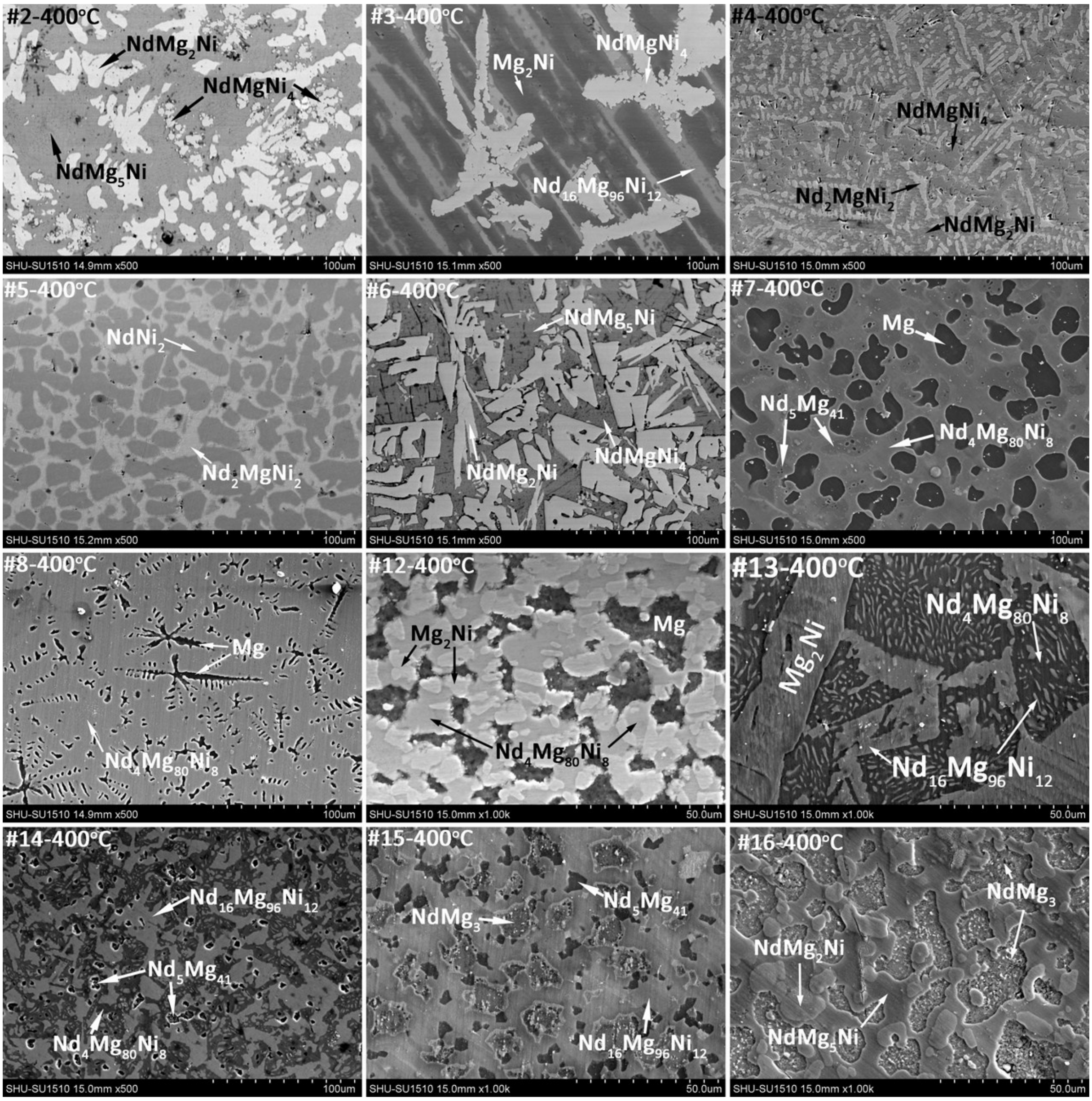

Fig. S2. (a) The SEM images of the samples annealed at 400 °C

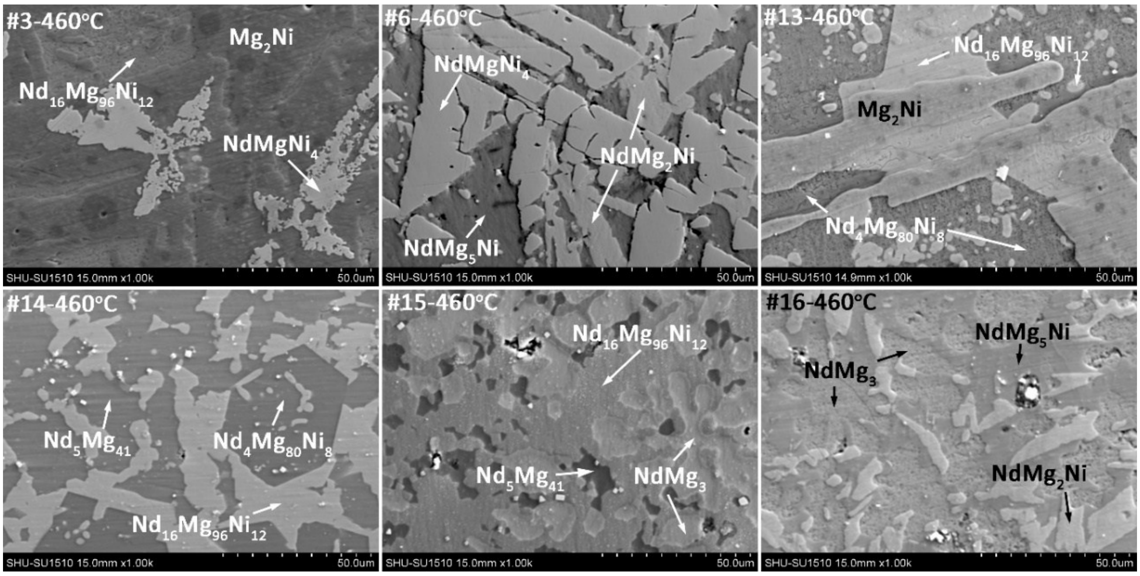

Fig. S2. (b) The SEM images of the samples annealed at 460 °C

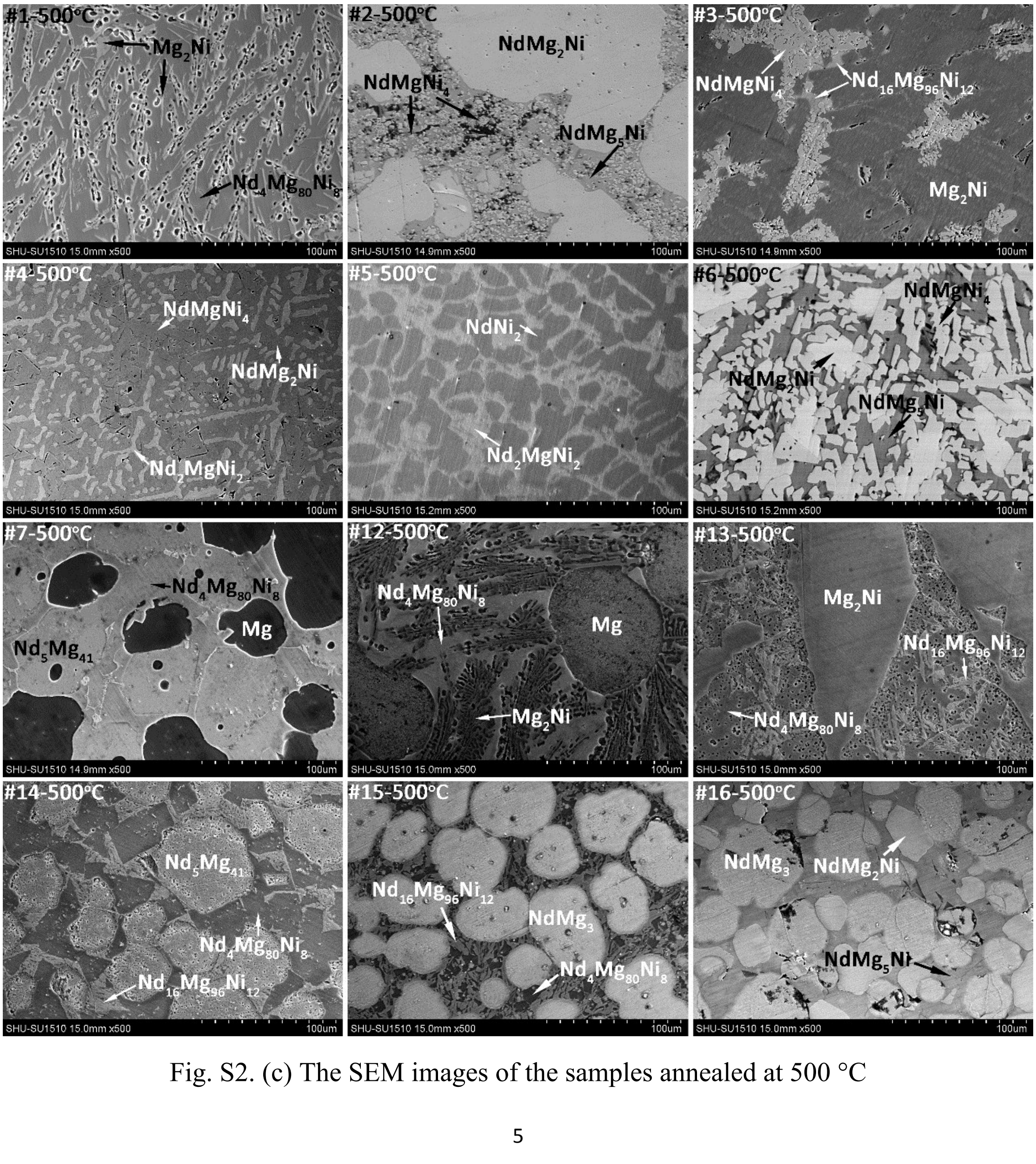

Fig. S2. (c) The SEM images of the samples annealed at 500 °C

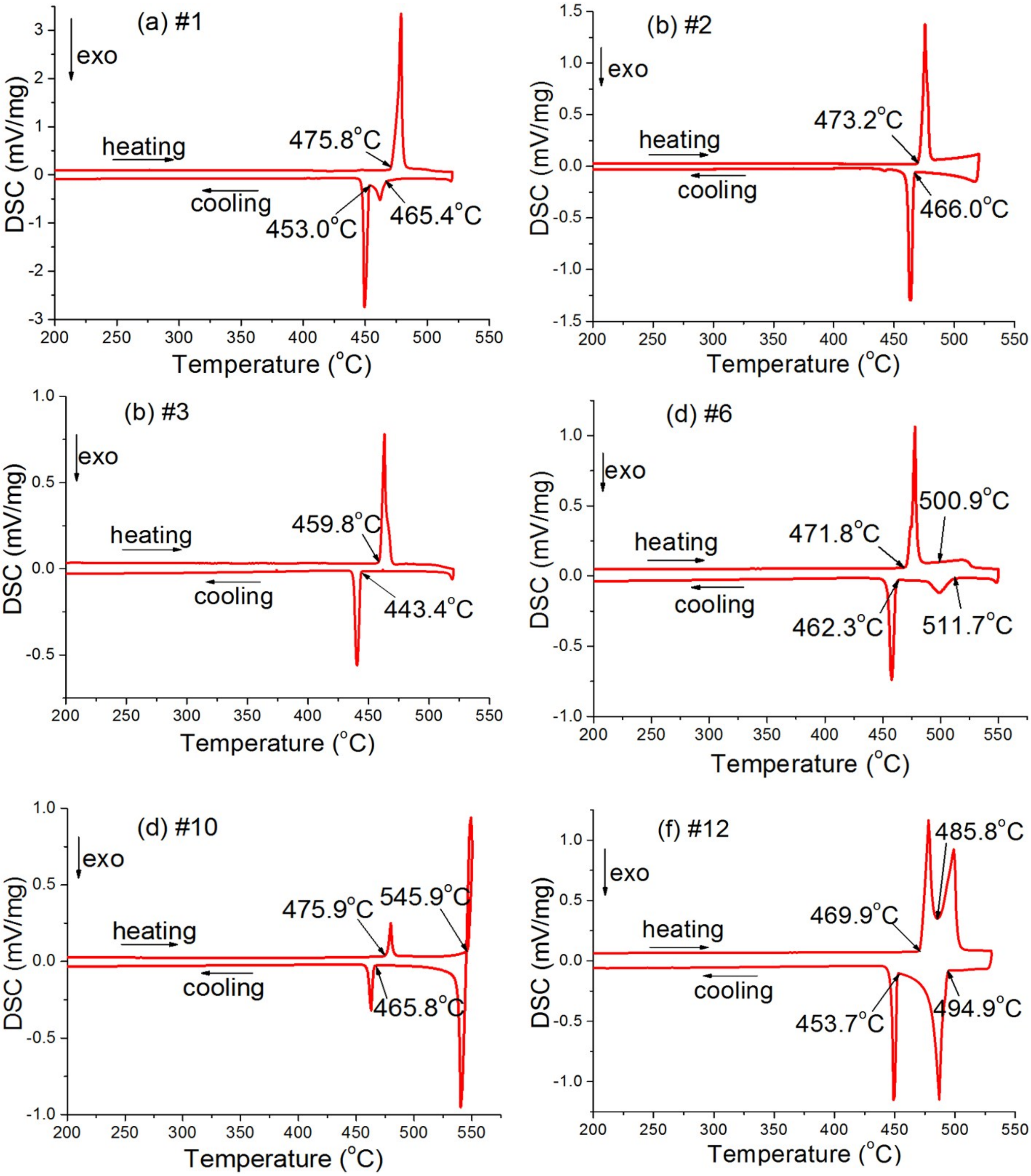

Fig. S3. The DSC curves of annealed alloys with heating and cooling rate of 5 °C /min

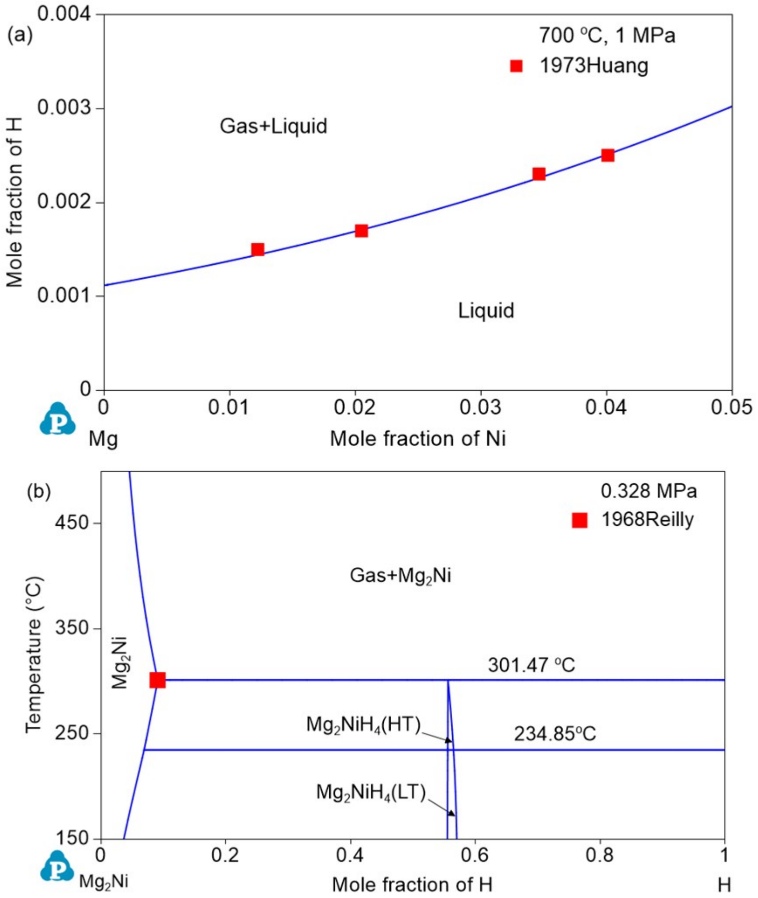

Fig. S4. (a) The calculated phase boundary of L/L+Gas in Mg−Ni−H system compared with experimental data, and (b) the calculated vertical section of Mg_2Ni−H at 0.328 MPa

First-Principles Calculations Conditions for Formation Enthalpies of Compounds:

The parameters setting in evaluation of the total energies of phases are listed in Table S1. The total energies of other phases were calculated after geometry optimizations with unit cell volume, shape and atomic positions fully relaxing. However, for Nd, $NdMg_5Ni$ and $Nd_{16}Mg_{96}Ni_{12}$ phases, the convergence of the self-consistent field cycle can be difficult to achieve. A solid has a certain equilibrium volume V_0, and the energy increase as volume is increased or decreased a small amount from that value. Therefore, we optimized the atomic positions at fixed cell volumes and calculated the corresponding total energies. Then the total energy dependence on cell volume was fitted by the simplest Murnaghan equation of state,

$$E = E_0 + K_0\left[V_0 - V + V\ln\left(\frac{V}{V_0}\right)\right] \tag{S.1}$$

where K_0 is the isothermal bulk modulus, and the E_0 is the equilibrium total energy. The fitted curves are shown in Fig. S5. The optimized structure information are also shown comparing with experimental data in Table S1.

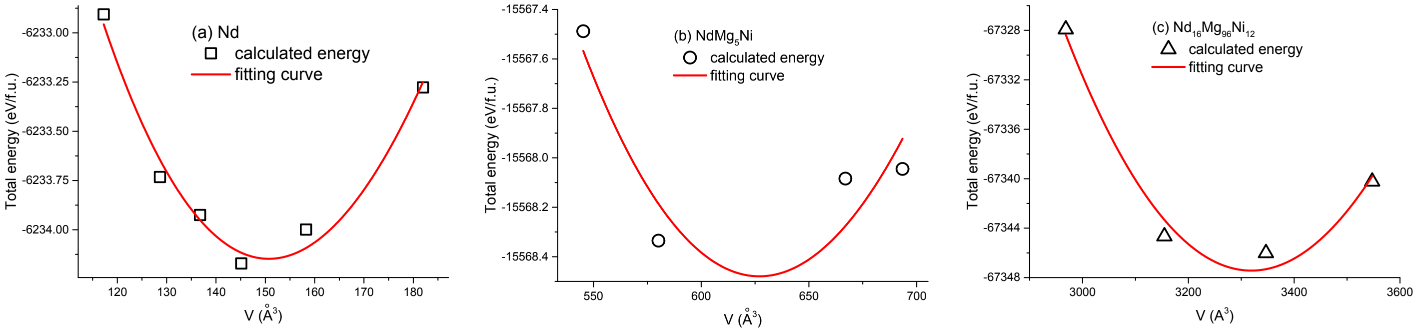

Fig. S5. The fitting curves of the total energies for (a) Nd, (b) $NdMg_5Ni$ and (c) $Nd_{16}Mg_{96}Ni_{12}$

Table S1. The conditions for the first-principles calculation

Phase	Calculated conditions		Calculated results			
	k point	Cut-off energy (eV)	Lattice parameter (Å)		Total Energy (eV/f.u.)	ΔH_f (kJ/mol-atom)
			Opt.	Exp.		
Mg	7×7×4	400	*a*=3.23501, *c*=5.26135	*a*=3.2094, *c*=5.2103 [1]	−973.9423	
Ni	8×8×8	400	*a*=3.52773	*a*=3.524 [2]	−1354.3297	
Nd	6×6×2	360	*a*= 3.7312 *c*=12.0380	*a*=3.6582, *c*=11.7966 [3]	−1558.5468	
Mg_2Ni	6×6×2	400	*a*=5.16983, *c*=12.88976	*a*=5.205, *c*=13.236 [4]	−3302.8342	−19.93
$NdNi_5$	6×6×6	400	*a*=5.03235, *c*=4.08709	*a*=4.949~4.973 , *c*=3.974~4.0124 [5-9]	−8331.7105	−24.51
$NdMgNi_4$	4×4×4	400	*a*=7.16959	*a*=7.0988~7.1234 [10, 11]	−7951.7195	−30.88
$NdMg_2Ni_9$	6×6×2	400	*a*=4.89561, *c*=23.80639	*a*=4.896, c=23.842 [12]	−15698.8293	−27.65
$Nd_4Mg_{80}Ni_8$	2×2×2	400	*a*=11.2331	*a*=11.2743	−94987.7984	−3.802

			5	c=15.9170 [13]		
			c=16.43734			
$Nd_{16}Mg_{96}Ni_{12}$	1×1×1	400	a=15.6038 b=22.0448 c=9.6489	a=15.34197 b=21.67494 c=9.486856	−134694.8662	−6.110
$NdMg_5Ni$	4×2×1	400	a=4.5047, b=10.0393, c=13.8642	a=4.4799, b=9.9827, c=13.7854 [14]	−7784.2397	−22.89

Calculation Formulae for Hydriding/Dehydriding Kinetics and Calculated Results:

In our previous work [15-17], we have proposed a series of kinetic formulae concerning the kinetics of solid-gas reaction by assuming a specific rate-controlling step, such as surface penetration of hydrogen atoms, diffusion of hydrogen atoms through the hydride product layer to the hydride/metal interface, chemical reaction and nucleus formation producing hydride. When the rate-limiting step is the diffusion of hydrogen in the hydride, the integral form of formula for a spherical particle is

$$\xi = 1 - \left(1 - \sqrt{\frac{t}{t_{c(d)}}}\right)^3 \tag{S.2}$$

The differential form is

$$\frac{d\xi}{dt} = \frac{3}{2t_{c(d)}} \cdot \frac{(1-\xi)^{\frac{2}{3}}}{1-(1-\xi)^{\frac{1}{3}}} \tag{S.3}$$

With regard to the sample which has already been hydrogenated and a layer of hydride has been formed, intergrating Eq. (S.3) with the initial condition of $\xi=\xi_0$ when $t=t_0$, we have

$$\xi = 1 - \left(1 - \sqrt{\frac{t-t_0}{t_{c(d)}} + \left[1-(1-\xi_0)^{\frac{1}{3}}\right]^2}\right)^3 \tag{S.4}$$

When rate-limiting step is chemical reaction, the intergal form of formula is

$$\xi = 1 - \left(1 - \frac{t}{t_{c(cr)}}\right)^3 \tag{S.5}$$

where ξ is the reacted fraction, $t_{c(d)}$ is the characteristic reaction time representing the required time of a completely hydriding or dehydriding of the sample.

Using Eqs. (S.2), (S.4) or (S.5) to fit the experimental data, the t_c can be calculated. The corresponding squared correlation coefficient r^2 reflects the level of agreement between fitting curve and experimental data. Table S2 lists the calculated results for hydrogenation and dehydrogenation of $Nd_4Mg_{80}Ni_8$, $Nd_{16}Mg_{96}Ni_{12}$ and $Nd_{6.7}Mg_{90.5}Ni_{2.8}$ alloys.

Table S2. The regression results for hydriding and dehydriding reaction of $Nd_4Mg_{80}Ni_8$, $Nd_{16}Mg_{96}Ni_{12}$ and $Nd_{6.7}Mg_{90.5}Ni_{2.8}$ alloys at 350 °C

Alloys	Hydrogenation			Dehydrogenation		
	Rate-limiting step	t_c (min)	r^2	Rate-limiting step	t_c (min)	r^2
$Nd_4Mg_{80}Ni_8$	Diffusion (0≤ξ≤0.86)	2.2	0.96	Chemical reaction (0≤ξ≤1)	1.4	0.99
	Diffusion (0.86≤ξ≤1)	17.9	0.95			
$Nd_{16}Mg_{96}Ni_{12}$	Diffusion (0≤ξ≤0.98)	6.1	0.99	Chemical reaction (0≤ξ≤1)	1.9	0.99
$Nd_{6.7}Mg_{90.5}Ni_{2.8}$	Diffusion (0≤ξ≤0.85)	8.8	0.90	Chemical reaction (0≤ξ≤1)	4.0	0.98
	Diffusion (0.85≤ξ≤1)	52.6	0.92			

The Optimized Thermodynamic Parameters in Mg−Ni−Nd−H System

Functions: Note Ref.

$$G^{MgH_2} = -108422.153 + 495.654622T - 75T\ln T - 3.6920685\times10^{-16}T^2 + 5.93903667\times10^{-20}T^3 - 1.7334725\times10^{-8}T^{-1}$$ [40]

$$G^{Mg_2Ni} = -20320.4 + 138.49311T - 24.9354T\ln T - 0.001538T^2 + 133805T^{-1}$$ [21]

$$G^{MgNi_2} = -24688.46 + 147.27013T - 25.7998T\ln T - 0.00246496T^2 + 111575.5T^{-1}$$ [21]

Phases:

Gas: Model (H_2, H, Nd, Ni, H)

$$G_{H_2}^{Gas} = {}^{o}G_{H_2}^{Gas} + RT\ln(9.8692327\times10^{-6}P)$$ [57]

$$G_{H}^{Gas} = {}^{o}G_{H}^{Gas} + RT\ln(9.8692327\times10^{-6}P)$$ [57]

$G_{Nd}^{Gas} = {}^{\circ}G_{Nd}^{Gas} + RT\ln(9.8692327\times10^{-6}P)$	This work
$G_{Mg}^{Gas} = {}^{\circ}G_{Mg}^{Gas} + RT\ln(9.8692327\times10^{-6}P)$	[57]
$G_{Ni}^{Gas} = {}^{\circ}G_{Ni}^{Gas} + RT\ln(9.8692327\times10^{-6}P)$	[57]

Liquid: Model (Nd, Mg, Ni, H)

$G_{Nd}^{L} = {}^{\circ}G_{Nd}^{Liquid}$	[33]
$G_{Mg}^{L} = {}^{\circ}G_{Mg}^{Liquid}$	[33]
$G_{Ni}^{L} = {}^{\circ}G_{Ni}^{Liquid}$	[35]
$G_{H}^{L} = 0.5\,{}^{\circ}G_{H}^{Gas} + 8035 + 25T + 2TlnT$	[40]
${}^{0}L_{\mathrm{Mg},Ni}^{L} = -50910 + 25.79995T$	[21]
${}^{1}L_{\mathrm{Mg},Ni}^{L} = -14989.95 + 13.24788T$	[21]
${}^{0}L_{\mathrm{Mg},Nd}^{L} = -33208.7 + 10.8T$	This work
${}^{1}L_{\mathrm{Mg},Nd}^{L} = -15765.6$	This work
${}^{2}L_{\mathrm{Mg},Nd}^{L} = -17079$	This work
${}^{0}L_{Nd,Ni}^{L} = -166540 + 38.798T$	[37]
${}^{1}L_{Nd,Ni}^{L} = 34987 - 5.354T$	[37]
${}^{2}L_{Nd,Ni}^{L} = 24991$	[37]
${}^{0}L_{Ni,H}^{L} = -8690.93694 + 10.7429419T$	[42]
${}^{0}L_{\mathrm{Mg},H}^{L} = 13040.4878 - 3.9621749T$	[42]
${}^{0}L_{Mg,Ni,Nd}^{L} = -75460 + 20T$	This work
${}^{1}L_{Mg,Ni,Nd}^{L} = -45460 + 20T$	This work
${}^{2}L_{Mg,Ni,Nd}^{L} = -5000$	This work
${}^{0}L_{Mg,Ni,H}^{L} = -205000$	This work

${}^{1}L^{L}_{Mg,Ni,H} = -288000$ This work

${}^{2}L^{L}_{Mg,Ni,H} = 1076135$ This work

Hcp: (Mg, Ni, Nd)$_1$(H, Va)$_{0.5}$

$G^{Hcp}_{Nd:Va} = {}^{o}G^{Dhcp}_{Nd} + 303.4$ [33]

$G^{Hcp}_{Mg:Va} = {}^{o}G^{Hcp}_{Mg}$ [33]

$G^{Hcp}_{Ni:Va} = {}^{o}G^{Hcp}_{Ni}$ [21]

$G^{Hcp}_{Mg:H} = G^{MgH_2} - 0.75\,{}^{o}G^{Gas}_{H_2} + 87394.9 - 122.339T$ [40]

$G^{Hcp}_{Ni:H} = {}^{o}G^{Fcc}_{Ni} + 0.25\,{}^{o}G^{Gas}_{H_2} + 50000$ This work

${}^{0}L^{Hcp}_{Mg,Ni:Va} = 80T$ [21]

${}^{0}L^{Hcp}_{Mg,Nd:Va} = -13800 + 2.5T$ This work

${}^{1}L^{Hcp}_{Mg,Nd:Va} = -8000$ This work

Dhcp: Model (Nd, Ni)$_1$(H, Va)$_2$

$G^{Dhcp}_{Nd:Va} = {}^{o}G^{Dhcp}_{Nd}$ [33]

$G^{Dhcp}_{Mg:Va} = {}^{o}G^{Hcp}_{Mg} + 303.4$ [33]

$G^{Dhcp}_{Ni:Va} = {}^{o}G^{Dhcp}_{Ni} + 500$ [35]

$G^{Dhcp}_{Nd:H} = {}^{o}G^{Dhcp}_{Nd} + {}^{o}G^{Gas}_{H_2} - 146740.654 + 118.589T$ This work

${}^{0}L^{Dhcp}_{Mg,Nd:Va} = 45066.1 - 19.585T$ [33]

${}^{1}L^{Dhcp}_{Mg,Nd:Va} = 54492.8 - 9.86T$ [33]

${}^{0}L^{Dhcp}_{Nd,Ni:Va} = -10000$ [35]

Bcc: Model (Nd, Mg, Ni)$_1$(H, Va)$_3$

$G^{Bcc}_{Nd:Va} = {}^{o}G^{Bcc}_{Nd}$ [33]

$G^{Bcc}_{Mg:Va} = {}^{o}G^{Bcc}_{Mg}$ [33]

$G^{Bcc}_{Ni:Va} = {}^{o}G^{Bcc}_{Ni}$ [35]

$G^{Bcc}_{Nd:H} = {}^{o}G^{Bcc}_{Nd} + 1.5\,{}^{o}G^{Gas}_{H_2} - 135207.418 + 108.37T$ This work

${}^{0}L^{Bcc}_{Nd,Ni:Va} = -8500$ [35]

${}^{0}L^{Bcc}_{Mg,Nd:Va} = -26221.4 + 3.9T$ [33]

${}^{1}L^{Bcc}_{Mg,Nd:Va} = -28096.4 + 10.3T$ [33]

${}^{2}L^{Bcc}_{Mg,Nd:Va} = -15898.5$ [33]

Fcc: Model (Ni, Mg, Nd)$_1$(H, Va)$_1$

$G^{Fcc}_{Ni:Va} = {}^{o}G^{Fcc}_{Ni}$ [21]

$G^{Fcc}_{Mg:Va} = {}^{o}G^{Fcc}_{Mg}$ [21]

$G^{Fcc}_{Nd:Va} = {}^{o}G^{Fcc}_{Nd}$ [35]

$G^{Fcc}_{Ni:H} = {}^{o}G^{Fcc}_{Ni} + 0.5\,{}^{o}G^{Gas}_{H_2} - 3120.7324 + 180.5062T - 16.255T\ln T + 6.052879\times10^{-4}T^2$ [42]

$G^{Fcc}_{Nd:H} = {}^{o}G^{Fcc}_{Nd} + 0.5\,{}^{o}G^{Gas}_{H_2} + 50000$ This work

$G^{Fcc}_{Mg:H} = G^{MgH_2} - 0.5\,{}^{o}G^{Gas}_{H_2} + 80T$ [40]

${}^{0}L^{Fcc}_{Nd,Ni:Va} = 100000$ [35]

${}^{0}L^{Fcc}_{Mg,Ni:Va} = 80T$ [21]

${}^{0}T^{Fcc}_{C\,Ni:Va} = 633$ [42]

${}^{0}\beta^{Fcc}_{Ni:Va} = 0.52$ [42]

NdMg: Model (Mg, Ni, Nd)$_{0.5}$(Mg, Ni, Nd)$_{0.5}$(H, Va)$_3$

$G^{NdMg}_{Mg:Mg:Va} = 0$ [33]

$G^{NdMg}_{Nd:Nd:Va} = 0$ [33]

$G^{NdMg}_{Mg:Nd:Va} = -30734.3 + 7.42174T$ [33]

$G^{NdMg}_{Nd:Mg:Va} = -30734.3 + 7.42174T$ [33]

${}^{0}L^{NdMg}_{Mg,Nd:Nd:Va} = -20304.5$ [33]

$^{1}L^{NdMg}_{Mg,Nd:Nd:Va} = 8287.52$ [33]

$^{0}L^{NdMg}_{Nd:Mg,Nd:Va} = -20304.5$ [33]

$^{1}L^{NdMg}_{Nd:Mg,Nd:Va} = 8287.52$ [33]

$NdMg_2$: Model $(Mg)_2(Nd)_1$

$G^{NdMg_2}_{Mg:Nd} = 2\,^{\circ}G^{Hcp}_{Mg} + {}^{\circ}G^{Dhcp}_{Mg} - 45530 + 9T$ [33]

$NdMg_3$: Model $(Mg, Ni)_2(Nd, Mg)_1$

$G^{NdMg_3}_{Mg:Mg} = 4\,^{\circ}G^{Hcp}_{Mg} + 12400 - 8.4T$ [33]

$G^{NdMg_3}_{Mg:Nd} = 3\,^{\circ}G^{Hcp}_{Mg} + {}^{\circ}G^{Dhcp}_{Nd} - 75831.5 + 26.9T$ [33]

$^{0}L^{NdMg_3}_{Mg:Mg,Nd} = 7999.8$ [33]

Nd_5Mg_{41}: Model $(Mg, Nd)_{41}(Nd, Mg, Ni)_5$

$G^{Nd_5Mg_{41}}_{Mg:Mg} = 46\,^{\circ}G^{Hcp}_{Mg} + 138000$ [33]

$G^{Nd_5Mg_{41}}_{Nd:Nd} = 46\,^{\circ}G^{Hcp}_{Nd} + 138000$ [33]

$G^{Nd_5Mg_{41}}_{Mg:Nd} = 41\,^{\circ}G^{Hcp}_{Mg} + 5\,^{\circ}G^{Dhcp}_{Nd} - 459385.6 + 217.3T$ [33]

$G^{Nd_5Mg_{41}}_{Nd:Mg} = 5\,^{\circ}G^{Hcp}_{Mg} + 41\,^{\circ}G^{Dhcp}_{Nd} + 459385.6 - 217.3T$ [33]

$G^{Nd_5Mg_{41}}_{Mg:Ni} = 41\,^{\circ}G^{Hcp}_{Mg} + 5\,^{\circ}G^{Fcc}_{Ni} + 10T$ This work

$^{0}L^{Nd_5Mg_{41}}_{Mg,Nd:Mg} = -51679.8 + 10.2T$ [33]

$^{0}L^{Nd_5Mg_{41}}_{Mg,Nd:Nd} = -51679.8 + 10.2T$ [33]

$^{0}L^{Nd_5Mg_{41}}_{Mg:Mg,Nd} = -56137.8 + 3.7T$ [33]

$^{0}L^{Nd_5Mg_{41}}_{Nd:Mg,Nd} = -56137.8 + 3.7T$ [33]

Mg_2Ni: Model $(Mg)_{0.6667}(Ni)_{0.3333}(H, Va)_{0.3333}$

$G^{Mg_2Ni}_{Mg:Ni:Va} = G^{Mg_2Ni}$ [21]

$G^{Mg_2Ni}_{Mg:Ni:H} = G^{Mg_2Ni} + 0.16665\,^{\circ}G^{Gas}_{H_2} - 5832.3393 + 14.11655T$ This work

$MgNi_2$: Model $(Mg, Ni)_{0.3333}(Ni, Mg)_{0.6667}$

$$G^{MgNi_2}_{Mg:Ni} = G^{MgNi_2}$$ [21]

$$G^{MgNi_2}_{Mg:Mg} = {}^{0}G^{Hcp}_{Mg} + 764.706 + 20.5885T$$ [21]

$$G^{MgNi_2}_{Ni:Mg} = 0.6667\,{}^{0}G^{Hcp}_{Mg} + 0.3333\,{}^{0}G^{Fcc}_{Ni} + 1000$$ [21]

$$G^{MgNi_2}_{Ni:Ni} = {}^{0}G^{Fcc}_{Ni} + 5254.902 + 6.862745T$$ [21]

Nd_3Ni: Model $(Nd)_{0.75}(Ni)_{0.25}$

$$G^{Nd_3Ni}_{Nd:Ni} = 0.75\,{}^{0}G^{Dhcp}_{Nd} + 0.25\,{}^{0}G^{Fcc}_{Ni} - 28093 + 7.967T$$ [35]

Nd_7Ni_3: Model $(Nd)_{0.7}(Ni)_{0.3}$

$$G^{Nd_7Ni_3}_{Nd:Ni} = 0.7\,{}^{0}G^{Dhcp}_{Nd} + 0.3\,{}^{0}G^{Fcc}_{Ni} - 33789 + 10.595T$$ [35]

NdNi: Model $(Nd)_{0.5}(Ni)_{0.5}$

$$G^{NdNi}_{Nd:Ni} = 0.5\,{}^{0}G^{Dhcp}_{Nd} + 0.5\,{}^{0}G^{Fcc}_{Ni} - 46879 + 12.065T$$ [35]

$NdNi_2$: Model $(Nd)_{0.3333}(Ni)_{0.6667}$

$$G^{NdNi_2}_{Nd:Ni} = 0.3333\,{}^{0}G^{Dhcp}_{Nd} + 0.6667\,{}^{0}G^{Fcc}_{Ni} - 36591.721 + 4.306T$$ This work

$NdNi_3$: Model $(Nd)_{0.25}(Ni)_{0.75}$

$$G^{NdNi_3}_{Nd:Ni} = 0.25\,{}^{0}G^{Dhcp}_{Nd} + 0.75\,{}^{0}G^{Fcc}_{Ni} - 32262.113 + 3.493T$$ This work

Nd_2Ni_7: Model $(Nd)_{0.2222}(Ni)_{0.7778}$

$$G^{Nd_2Ni_7}_{Nd:Ni} = 0.2222\,{}^{0}G^{Dhcp}_{Nd} + 0.7778\,{}^{0}G^{Fcc}_{Ni} - 30893.89 + 3.506T$$ This work

Nd_2Ni_{17}: Model $(Nd)_{0.1053}(Ni)_{0.8947}$

$$G^{Nd_2Ni_{17}}_{Nd:Ni} = 0.1053\,{}^{0}G^{Dhcp}_{Nd} + 0.8947\,{}^{0}G^{Fcc}_{Ni} - 16387.5 + 1.62603T$$ This work

$NdNi_5$: Model $(Nd)_{0.1667}(Ni)_{0.8333}(H, Va)_{0.5}$ Para. Set 1

$$G^{NdNi_5}_{Nd:Ni:Va} = 0.1667\,{}^{0}G^{Dhcp}_{Nd} + 0.8333\,{}^{0}G^{Fcc}_{Ni} - 28248.82 + 4.088T$$ Para. Set 1 This work

$$G^{NdNi_5}_{Nd:Ni:H} = 0.1667\,{}^{0}G^{Dhcp}_{Nd} + 0.8333\,{}^{0}G^{Fcc}_{Ni} + 0.25\,{}^{0}G^{Gas}_{H_2} - 36328 + 36T$$ Para. Set 1 This work

$${}^{0}L^{NdNi_5}_{Nd:Ni:H,Va} = 10000$$ Para. Set 1 This work

$${}^{1}L^{NdNi_5}_{Nd:Ni:H,Va} = 18000$$ Para. Set 1 This work

$NdMgNi_4$: Model $(Nd)_{0.1667}(Mg)_{0.1667}(Ni)_{0.6666}$ $(H, Va)_{0.6666}$

$$G^{NdMgNi_4}_{Nd:Mg:Ni:Va} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.1667\,{}^{\circ}G^{Hcp}_{Mg} + 0.6667\,{}^{\circ}G^{Fcc}_{Ni} - 37333.33 + 10.5T$$

This work

$$G^{NdMgNi_4}_{Nd:Mg:Ni:H} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.1667\,{}^{\circ}G^{Hcp}_{Mg} + 0.6667\,{}^{\circ}G^{Fcc}_{Ni} + 0.3333\,{}^{\circ}G^{Gas}_{H_2} - 30947.4 + 35.5T$$

This work

$${}^{0}L^{NdMgNi_4}_{Nd:Mg:Ni:H,Va} = -8000$$

This work

$${}^{1}L^{NdMgNi_4}_{Nd:Mg:Ni:H,Va} = 8000$$

This work

$NdMg_2Ni_9$: Model $(Nd)_{0.0833}(Mg)_{0.1667}(Ni)_{0.75}(H, Va)_{2.8333}$

$$G^{NdMg_2Ni_9}_{Nd:Mg:Ni:Va} = 0.0833\,{}^{\circ}G^{Dhcp}_{Nd} + 0.1667\,{}^{\circ}G^{Hcp}_{Mg} + 0.75\,{}^{\circ}G^{Fcc}_{Ni} - 23713.34 + 5.09T$$

This work

$$G^{NdMg_2Ni_9}_{Nd:Mg:Ni:H} = 0.0833\,{}^{\circ}G^{Dhcp}_{Nd} + 0.1667\,{}^{\circ}G^{Hcp}_{Mg} + 0.75\,{}^{\circ}G^{Fcc}_{Ni} + 1.4167\,{}^{\circ}G^{Gas}_{H_2} - 30475 + 118.5T$$

This work

Nd_2MgNi_2: Model $(Nd)_{0.4}(Mg)_{0.2}(Ni)_{0.4}$

$$G^{Nd_2MgNi_2}_{Nd:Mg:Ni} = 0.4\,{}^{\circ}G^{Dhcp}_{Nd} + 0.2\,{}^{\circ}G^{Hcp}_{Mg} + 0.4\,{}^{\circ}G^{Fcc}_{Ni} - 51000.37 + 22.84T$$

This work

$NdMg_2Ni$: Model $(Nd)_{0.25}(Mg)_{0.5}(Ni)_{0.25}$

$$G^{NdMg_2Ni}_{Nd:Mg:Ni} = 0.25\,{}^{\circ}G^{Dhcp}_{Nd} + 0.5\,{}^{\circ}G^{Hcp}_{Mg} + 0.25\,{}^{\circ}G^{Fcc}_{Ni} - 43264.12 + 9.7T + 2064.75\ln T$$

This work

$Nd_4Mg_{80}Ni_8$: Model $(Nd)_{0.04}(Mg)_{0.87}(Ni)_{0.09}$

$$G^{Nd_4Mg_{80}Ni_8}_{Nd:Mg:Ni} = 0.04\,{}^{\circ}G^{Dhcp}_{Nd} + 0.87\,{}^{\circ}G^{Hcp}_{Mg} + 0.09\,{}^{\circ}G^{Fcc}_{Ni} - 9292 + 9.36T - 0.7T\ln T + 9800T^{2}$$

This work

$Nd_{16}Mg_{96}Ni_{12}$: Model $(Nd, Ni)_{0.13}(Mg)_{0.77}(Ni)_{0.10}$

$$G^{Nd_{16}Mg_{96}Ni_{12}}_{Nd:Mg:Ni} = 0.13\,{}^{\circ}G^{Dhcp}_{Nd} + 0.77\,{}^{\circ}G^{Hcp}_{Mg} + 0.10\,{}^{\circ}G^{Fcc}_{Ni} - 16618.625 + 7.5T$$

This work

$$G^{Nd_{16}Mg_{96}Ni_{12}}_{Ni:Mg:Ni} = 0.77\,{}^{\circ}G^{Hcp}_{Mg} + 0.23\,{}^{\circ}G^{Fcc}_{Ni} + 14T$$

This work

$${}^{0}L^{Nd_{16}Mg_{96}Ni_{12}}_{Nd,Ni:Mg:Ni} = -17467.75 - 5.775T$$

This work

$NdMg_5Ni$: Model $(Nd)_{0.14}(Mg)_{0.72}(Ni)_{0.14}$

$$G^{NdMg_5Ni}_{Nd:Mg:Ni} = 0.14\,{}^{\circ}G^{Dhcp}_{Nd} + 0.72\,{}^{\circ}G^{Hcp}_{Mg} + 0.14\,{}^{\circ}G^{Fcc}_{Ni} - 18921.324 + 7.965T - 153458.05T^{-1}$$

This work

γ: Model $(Nd)_1(H, Va)_2$

$G^{\gamma}_{Nd:Va} = {}^{\circ}G^{Dhcp}_{Nd} + 800$ This work

$G^{\gamma}_{Nd:H} = {}^{\circ}G^{Dhcp}_{Nd} + {}^{\circ}G^{Gas}_{H_2} - 138675.944 + 104.16T$ This work

NdH_2: Mdoel $(Nd)_1(H, Va)_2(H, Va)_1$

$G^{NdH_2}_{Nd:H:H} = {}^{\circ}G^{Dhcp}_{Nd} + 1.5\,{}^{\circ}G^{Gas}_{H_2} - 186000 + 157T$ This work

$G^{NdH_2}_{Nd:H:Va} = {}^{\circ}G^{Dhcp}_{Nd} + {}^{\circ}G^{Gas}_{H_2} - 187451.375 + 124.5T$ This work

$G^{NdH_2}_{Nd:Va:Va} = {}^{\circ}G^{Dhcp}_{Nd} + 50000$ This work

$G^{NdH_2}_{Nd:Va:H} = {}^{\circ}G^{Dhcp}_{Nd} + 0.5\,{}^{\circ}G^{Gas}_{H_2} - 100000 + 140T$ This work

$NdNi_5H_3$: Model $(Nd)_{0.1667}(Ni)_{0.8333}(H)_{0.5}(H, Va)_1$ Para. Set 1

$G^{NdNi_5H_3}_{Nd:Ni:H:Va} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.25\,{}^{\circ}G^{Gas}_{H_2} - 36328 + 36T$ Para. Set 1 This work

$G^{NdNi_5H_3}_{Nd:Ni:H:H} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.75\,{}^{\circ}G^{Gas}_{H_2}$ Para. Set 1 This work
$-41168.616 + 87.596T$

${}^{0}L^{NdNi_5H_3}_{Nd:Ni:H:H,Va} = -423.529 - 2.941T$ Para. Set 1 This work

${}^{1}L^{NdNi_5H_3}_{Nd:Ni:H:H,Va} = 4000$ Para. Set 1 This work

$NdNi_5H_6$: Model $(Nd)_{0.1667}(Ni)_{0.8333}(H)_{0.5}(H, Va)_1$ Para. Set 1

$G^{NdNi_5H_6}_{Nd:Ni:H:Va} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.25\,{}^{\circ}G^{Gas}_{H_2} - 36328 + 36T$ Para. Set 1 This work

$G^{NdNi_5H_6}_{Nd:Ni:H:H} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.75\,{}^{\circ}G^{Gas}_{H_2}$ Para. Set 1 This work
$-41168.616 + 87.596T$

${}^{0}L^{NdNi_5H_6}_{Nd:Ni:H:H,Va} = -5107.104 - 14.408T + 0.03488T^2$ Para. Set 1 This work

${}^{1}L^{NdNi_5H_6}_{Nd:Ni:H:H,Va} = -15764.706 + 29.41T$ Para. Set 1 This work

$NdNi_5H_x$: Model $(Nd)_{0.1667}(Ni)_{0.8333}(H, Va)_{0.5}(H, Va)_1$ Para. Set 2

$G^{NdNi_5H_x}_{Nd:Ni:Va:Va} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} - 28248.82 + 4.088T$ Para. Set 2 This work

$G^{NdNi_5H_x}_{Nd:Ni:H:Va} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.25\,{}^{\circ}G^{Gas}_{H_2} - 36128 + 36T$ Para. Set 2 This work

$G^{NdNi_5H_x}_{Nd:Ni:Va:H} = 0.1667\,{}^{\circ}G^{Dhcp}_{Nd} + 0.8333\,{}^{\circ}G^{Fcc}_{Ni} + 0.5\,{}^{\circ}G^{Gas}_{H_2}$ Para. Set 2 This work
$-41820.4 + 59.8T$

$$G_{Nd:Ni:H:H}^{NdNi_5H_x} = 0.1667\,{}^{o}G_{Nd}^{Dhcp} + 0.8333\,{}^{o}G_{Ni}^{Fcc} + 0.75\,{}^{o}G_{H_2}^{Gas} -45390.2 + 97.4T$$

Para. Set 2 This work

$${}^{0}L_{Nd:Ni:H,Va:Va}^{NdNi_5H_x} = 9000$$

Para. Set 2 This work

$${}^{1}L_{Nd:Ni:H,Va:Va}^{NdNi_5H_x} = 26303.667 - 13.333T$$

Para. Set 2 This work

$${}^{0}L_{Nd:Ni:H,Va:H}^{NdNi_5H_x} = -3000$$

Para. Set 2 This work

$${}^{1}L_{Nd:Ni:H:H,Va}^{NdNi_5H_x} = 11000$$

Para. Set 2 This work

$${}^{0}L_{Nd:Ni:Va:H,Va}^{NdNi_5H_x} = 23000$$

Para. Set 2 This work

MgH_2: Model $(Mg)_2(H)_1$

$$G_{Mg:H}^{MgH_2} = G^{MgH_2}$$

[40]

H_Mg_2NiH_4: Model $(Mg)_2(Ni)_1(H, Va)_1$

$$G_{Mg:Ni:H}^{Mg_2NiH_4} = 3G^{Mg_2Ni} + 2\,{}^{o}G_{H_2}^{Gas} - 136003.983 + 350.04T -13.7301T\ln T - 0.01299T^2$$

This work

$$G_{Mg:Ni:Va}^{Mg_2NiH_4} = 3G^{Mg_2Ni} + 90T$$

This work

L_Mg_2NiH_4: Model $(Mg)_2(Ni)_1(H, Va)_1$

$$G_{Mg:Ni:H}^{Mg_2NiH_4} = 3G^{Mg_2Ni} + 2\,{}^{o}G_{H_2}^{Gas} - 144003.983 + 365.788T -13.7301T\ln T - 0.01299T^2$$

This work

$$G_{Mg:Ni:Va}^{Mg_2NiH_4} = 3G^{Mg_2Ni} + 90T$$

This work

$NdMgNi_4H_4$: Model $(Nd)_{0.1667}(Mg)_{0.1667}(Ni)_{0.6666}(H, Va)_{0.6666}$

$$G_{Nd:Mg:Ni:Va}^{NdMgNi_4H_4} = 0.1667\,{}^{o}G_{Nd}^{Dhcp} + 0.1667\,{}^{o}G_{Mg}^{Hcp} + 0.6667\,{}^{o}G_{Ni}^{Fcc} -17333.33 + 10.5T$$

This work

$$G_{Nd:Mg:Ni:\mathrm{H}}^{NdMgNi_4H_4} = 0.1667\,{}^{o}G_{Nd}^{Dhcp} + 0.1667\,{}^{o}G_{Mg}^{Hcp} + 0.6667\,{}^{o}G_{Ni}^{Fcc} +0.3333\,{}^{o}G_{H_2}^{Gas} - 45947.4 + 35.5T$$

This work

$${}^{1}L_{Nd:Mg:Ni:\mathrm{H}}^{NdMgNi_4H_4} = -14000$$

This work

$NdMg_2Ni_9H_{12}$: Model $(Nd)_{0.0833}(Mg)_{0.1667}(Ni)_{0.75}(H, Va)_{2.8333}$

$$G_{Nd:Mg:Ni:Va}^{NdMg_2Ni_9H_{12}} = 0.0833\,{}^{o}G_{Nd}^{Dhcp} + 0.1667\,{}^{o}G_{Mg}^{Hcp} + 0.75\,{}^{o}G_{Ni}^{Fcc} -21713.34 + 5.09T$$

This work

$$G^{NdMg_2Ni_9H_{12}}_{Nd:Mg:Ni:H} = 0.0833\,{}^{o}G^{Dhcp}_{Nd} + 0.1667\,{}^{o}G^{Hcp}_{Mg} + 0.75\,{}^{o}G^{Fcc}_{Ni} + 1.4167\,{}^{o}G^{Gas}_{H_2} - 41475 + 118.5T$$

This work

$${}^{0}L^{NdMg_2Ni_9H_{12}}_{Nd:Mg:Ni:H,Va} = -31063.75 + 83.75T$$

This work

$${}^{1}L^{NdMg_2Ni_9H_{12}}_{Nd:Mg:Ni:H,Va} = 2000$$

This work

Note: Temperature *T* in Kelvin. The Gibbs energies for the pure elements are from the SGTE compilation [18]. The thermodynamic parameters in the Mg−Ni and Nd−Ni systems are taken from Ref. [19] and [20], respectively. The thermodynamic description of Nd−Mg is mainly based on the evaluation of Qi. et al. [21]. In order to improve the agreement of calculated phase boundary between Liquid and Hcp with the experimental data, the parameters of Liquid and Hcp were slightly modified in present work.

CIF File of $Nd_{16}Mg_{96}Ni_{12}$

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_cell_length_b    21.67494(16)
_cell_length_c    9.486856(67)
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_cell_angle_beta    90
_cell_angle_gamma 90
_cell_volume 3154.722(40)
_symmetry_space_group_name_H-M Cmc21

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_symmetry_equiv_pos_as_xyz
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    '-x, y, z'
    '-x+1/2, -y+1/2, z+1/2'
```

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    'x, -y, z+1/2'
    'x, y, z'
    'x+1/2, -y+1/2, z+1/2'
    'x+1/2, y+1/2, z'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_B_iso_or_equiv
Mg1 Mg     8 0.61974(88) 0.14089(60) 0.7458(43) 1 1.52(11)
Mg2 Mg     8 0.827764(73) 0.65786(58) 0.25242(34) 1 1.52(11)
Mg3 Mg     8 0.273528(96) 0.38488(50) 0.03793(10) 1 1.52(11)
Mg4 Mg     8 0.15249(81) 0.797061(41) 0.2286(21) 1 1.52(11)
Mg5 Mg     8 0.3424(11) 0.24827(93) 0.94987(10) 1 1.52(11)
Mg6 Mg     8 0.16928(37) 0.24102(99) 0.0845(16) 1 1.52(11)
Mg7 Mg     8 0.61657(78) 0.4988(16) 0.4836(25) 1 1.52(11)
Mg8 Mg     4 0.5 0.01007(98) 0.7727(44) 1 1.52(11)
Mg9 Mg     4 0.5 0.25919(93) 0.7398(42) 1 1.52(11)
Mg10 Mg     8 0.87875(95) 0.88552(57) 0.7277(24) 1 1.52(11)
Mg11 Mg     4 0 0.00408(45) 0.26460(38) 1 1.52(11)
Mg12 Mg     4 0 0.294974(72) 0.9251(25) 1 1.52(11)
Mg13 Mg     8 0.393131(75) 0.92322(99) 0.9619(16) 1 1.52(11)
Mg14 Mg     8 0.899059(59) 0.43741(94) 0.52098(14) 1 1.52(11)
Ni1 Ni     8 0.371933(49) 0.578396(32) 0.75597(14) 1 1.28(13)
Ni2 Ni     4 0 0.386425(41) 0.72940(17) 1 1.28(13)
```

Nd1 Nd 4 0 0.86852(46) 0.4501(11) 1 1.199(52)

Nd2 Nd 8 0.26581(13) 0.000928(58) 0.7572(12) 1 1.199(52)

Nd3 Nd 4 0 0.86783(45) 0.0573(11) 1 1.199(52)

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