

formation of nitrite as a reaction product in the nitrate melts results in a competition for additional carboxylic acid salt. The reactions with formate are more rapid than those with acetate, and caution is recommended in studying these systems.

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The Reaction of Hydrogen with Alloys of Magnesium and Nickel and the Formation of Mg_2NiH_4 ¹

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In the Mg–Ni system two intermetallic compounds are formed: Mg_2Ni and $MgNi_2$. $MgNi_2$ did not react with H_2 at pressures up to 400 psia and temperatures to 350°; however, Mg_2Ni reacted readily with H_2 at 300 psia and 325°. The product of the reaction was a new ternary hydride with the formula Mg_2NiH_4 . The reaction was reversible and upon decomposition the original starting material was regenerated. The X-ray diffraction pattern of the product was indexed. Several pressure–composition isotherms were obtained. The dissociation pressure of the hydride was found to obey the relationship $\log P_{atm} = (-3360/T) + 6.389$ from which thermodynamic data were calculated. In the presence of excess Mg the pressure–composition isotherm exhibited two plateaus; the lower plateau is attributed to the formation of MgH_2 as evidenced by X-ray diffraction data and thermodynamic considerations. The presence of Mg_2Ni appeared to have a catalytic effect on the formation of MgH_2 .

A previous article has described the reaction of hydrogen with magnesium–copper alloys.² In that article it was noted that the work was undertaken as part of an energy-storage program investigating the possibility of using reversible metal hydrides as a convenient and cheap means of storing hydrogen which is ultimately evolved and used as a fuel. This paper extends the discussion to the reaction of hydrogen with magnesium–nickel alloys at elevated temperatures and pressures. The system was found to be similar in some, but not all, respects to the Mg–Cu–H system.

Experimental Section

The materials used in this investigation were hydrogen gas obtained from the Matheson Co., Gold Label grade, having an assay of >99.99% H_2 ; zone-refined Mg rod, 0.25 in. in diameter and assaying 99.99% Mg with the major impurities being 20 ppm Fe and 20 ppm Zn; and nickel rod, 0.25 in. in diameter which assayed 99.99% Ni.

Although the procedure and apparatus were the same as that previously described in detail,³ a brief summary may be helpful. The Mg–Ni alloys were prepared in an induction furnace under argon. The alloys were then transferred to a drybox, pulverized to –25 mesh, and introduced into a stainless steel high-pressure reactor. The reactor was removed from the drybox and attached to an experimental rack. The alloy samples were hydrided by exposing them to H_2 at ~350 psia at temperatures up to 350°. The hydrided alloys could be decomposed by reducing the H_2 overpressure through the use of an evacuated gas reservoir or by outgassing under a dynamic vacuum.

Results and Discussion

Mg forms two intermetallic compounds with Ni, Mg_2Ni and $MgNi_2$.³ Within the limits of the experi-

mental conditions, *i.e.*, a maximum temperature of 350° and a maximum pressure of 400 psia, $MgNi_2$ did not react with H_2 . However, Mg_2Ni reacted at a temperature of 325° at an H_2 pressure of 300 psia. Although initially the rate of reaction was somewhat slow, the kinetics improved markedly after several cycles of hydriding and decomposition, and after such pretreatment the alloys reacted readily at temperatures as low as 200° and an H_2 pressure as low as 200 psia.

In Figure 1 are shown three pressure–composition isotherms for the system Mg_2Ni-H_2 . The initial composition of the sample was 45.9 wt % Mg and 54.6 wt % Ni; the theoretical composition of Mg_2Ni is 45.3 wt % Mg and 54.7 wt % Ni. The only phase initially present, as determined by an X-ray diffraction pattern of the sample, was Mg_2Ni . All of the isotherms ascend rapidly on the left indicating a narrow region where a solid solution of hydrogen in Mg_2Ni exists. This is followed by a wide plateau region, the initiation of which indicates the appearance of a new phase. To the right of the plateau each isotherm ascends very steeply. This portion of the isotherm is depicted as a dashed line because a small amount of solid hydride had to be decomposed before the first equilibrium point on the right could be defined and even a decomposition of a very small amount of material resulted in an equilibrium point on or near the plateau. The abrupt termination of the plateau indicates that the hydride formed has a definite stoichiometric composition. An X-ray diffraction pattern of the hydrided material showed no evidence of the presence of MgH_2 , $MgNi_2$, Ni, or any

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. J. Reilly and R. H. Wiswall, *Inorg. Chem.*, **6**, 2220 (1967).

(3) J. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

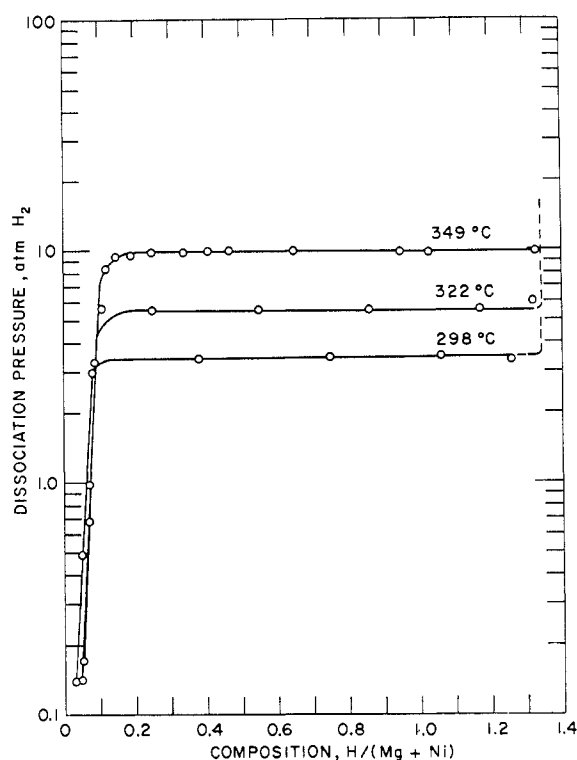


Figure 1.—Pressure-composition isotherm for the Mg₂Ni-H₂ system. The initial alloy composition is 45.9 wt % Mg and 54.6 wt % Ni.

known compound. Thus, on the basis of the stoichiometry of the system and X-ray studies, the reaction in the plateau region is believed to be



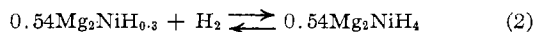
The product of the reaction had a rust-colored, non-metallic appearance. It reacted very slowly with water but vigorously with dilute nitric acid, evolving copious quantities of H₂. The product did not react with air in short-term exposures; however, one sample stored for several months in a stoppered bottle had apparently slowly oxidized, turning into a black nonreactive powder.

The crystal symmetry, as determined from the X-ray powder pattern, was tetragonal. The dimensions of the unit cell were $a = 6.464 \text{ \AA}$ and $c = 7.033 \text{ \AA}$. The measured density of the product was 2.57 g/cm^3 which when compared with the X-ray data yields a value of 4 molecules per unit cell (the actual calculated number was 4.07).

The dissociation pressures (plateau region) for reaction 1 found at each of a series of temperatures were (given as T (°C), P (atm)): 274, 1.77; 299, 3.24; 322, 5.59; 3.25, 5.95; 349, 9.71.

A semilog plot of these dissociation pressures *vs.* the reciprocal of the absolute temperature gave a straight line which obeyed the relationship $\log P_{\text{atm}} = (-A/T) + B$, where $A = 3360$ and $B = 6.389$.

An examination of Figure 1 shows that hydrogen dissolves in the Mg₂Ni phase to the extent that the ratio of $\text{H}/(\text{Mg} + \text{Ni}) \cong 0.1$; thus, eq 1 may be rewritten



The thermodynamic functions at a constant pressure of 1 atm of H₂ for reaction 2 calculated from the above dissociation pressure data are: $\overline{\Delta H}_{298^\circ\text{K}} = -15.4 \pm 1 \text{ kcal/mol}$ of H₂, $\overline{\Delta F}_{298^\circ\text{K}} = -6.7 \pm 1 \text{ kcal/mol}$ of H₂, and $\overline{\Delta S}_{298^\circ\text{K}} = -29.2 \pm 1.5 \text{ cal/deg mol}$ of H₂.

If Mg is present in the alloy in excess of the composition corresponding to Mg₂Ni, the pressure-composition isotherm exhibits two plateaus as shown in Figure 2.

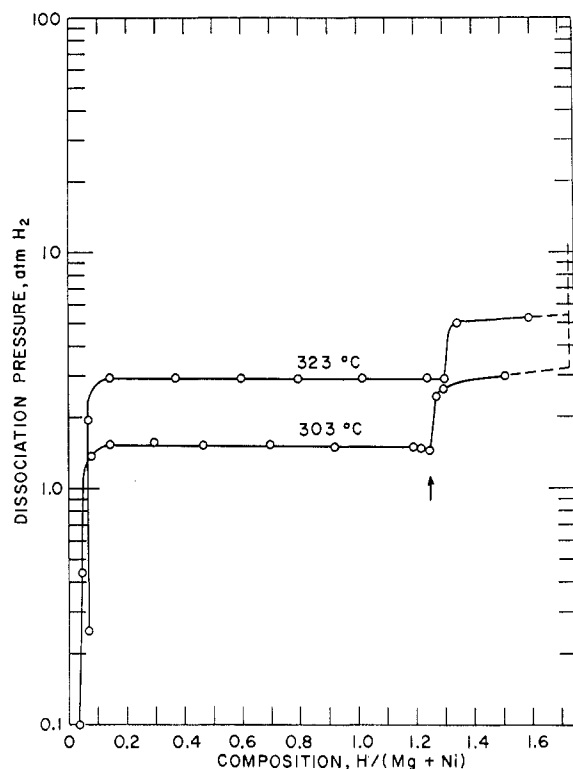
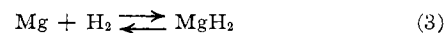


Figure 2.—Pressure-composition isotherm for the Mg₂Ni-Mg-H₂ system. The initial alloy composition is 72.9 wt % Mg and 25.2 wt % Ni. The arrow indicates predicted appearance of upper plateau.

The lower plateau is apparently due to the known reaction of Mg with H₂



This situation is very similar to the Mg-Cu system previously studied² in which excess Mg in an Mg₂Cu alloy forms MgH₂ and the system also exhibits two pressure plateaus. When all of the free Mg is exhausted, the second and higher plateau appears, which is due to reaction 1 of the intermetallic compound, Mg₂Ni, with H₂. An X-ray diffraction pattern taken of material whose composition corresponded to that of the lower plateau region ($\text{H}/(\text{Mg} + \text{Ni}) = 0.53$) has shown MgH₂, Mg₂Ni, and Mg to be present.

Even an alloy whose initial composition is only slightly on the Mg-rich side will give an isotherm whose shape is noticeably different from that of pure Mg₂Ni. This is illustrated in Figure 3 where the small shoulder in the isotherm is due to the presence of a small amount of MgH₂.

In these alloys the lengths of each pressure plateau are proportional to the relative amounts of free Mg

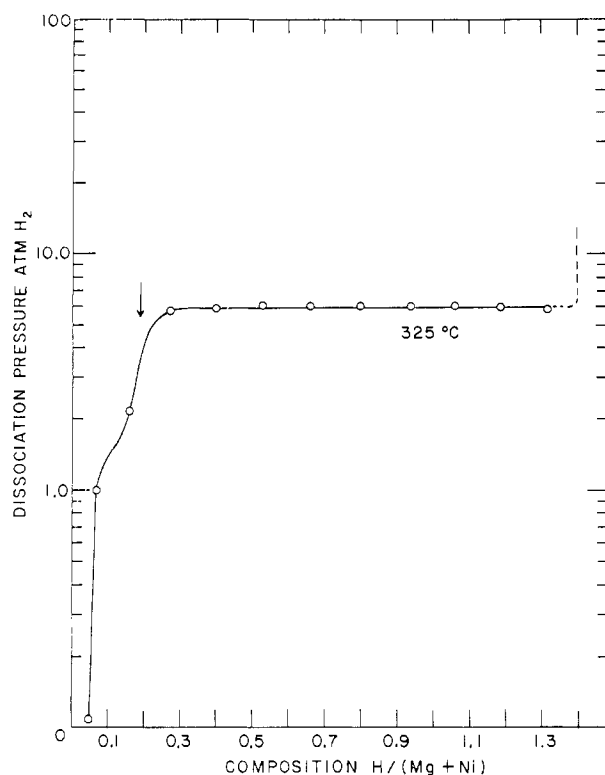


Figure 3.—Pressure-composition isotherm for Mg_2Ni with a small excess of Mg present. The initial alloy composition is 49.1 wt % Mg and 50.9 wt % Ni. The arrow indicates predicted appearance of upper plateau.

and Mg_2Ni initially present. The arrows shown in Figures 2 and 3 mark where the boundary between the upper and lower plateaus should occur as predicted by reactions 1 and 3. The calculations did not take into account the formation of solid solutions which occurs to some extent as indicated by the slope of the line connecting the two plateaus. As with Mg_2Cu , the presence of Mg_2Ni had a catalytic effect on the reaction of Mg with H_2 in Mg-rich alloys.

The dissociation pressures (plateau region) for MgH_2 in the presence of Mg_2Ni at various temperatures are (given as T ($^{\circ}C$), P (atm)): 276, 0.72; 300, 1.48; 324, 2.93; 350, 5.48.

A semilog plot of these dissociation pressures *vs.* the reciprocal of the absolute temperature yields a straight line obeying the relationship $\log P_{atm} = (-4045/T) + 7.224$. The thermodynamic functions calculated from

these data, assuming Mg_2Ni acts purely as a catalyst, are: $\overline{\Delta H}_{298^{\circ}K} = -18.5 \pm 1.0$ kcal/mol of H_2 , $\overline{\Delta F}_{298^{\circ}K} = -8.7 \pm 1.0$ kcal/mol of H_2 , and $\overline{\Delta S}_{298^{\circ}K} = -33.0 \pm 0.7$ cal/deg mol of H_2 . The above values are shown as partial molal quantities and refer to the reaction of 1 mol of H_2 at 1 atm pressure and at 298 $^{\circ}K$ with Mg saturated with hydrogen ($\sim MgH_{0.05}$) to form MgH_2 . The amount of hydrogen dissolving in the Mg_2Ni phase at the point where the MgH_2 phase appears is not considered since it is negligible when only small amounts of Mg_2Ni are present. These values are in good agreement with those obtained previously with Mg-Cu² alloys and with Mg^4 alone.

In order to obtain a further check on the validity of eq 1 and 2, several alloys of various compositions were hydrided and dehydrided several times and then finally contacted with H_2 for several days. The H_2 pressure over the alloy was held >200 psi above the hydride dissociation pressure. These samples were analyzed for hydrogen content and, as shown in Table I, the actual hydrogen contents are in good agreement with predicted values.

TABLE I
HYDROGEN CONTENT OF Mg-Ni ALLOYS

Expt no.	Initial alloy compn, wt %	Major initial phases present ^a	H/Mg	
			Exptl	Theoret
1	45.8 (Mg)	Mg_2Ni	1.95	2.00
	54.5 (Ni)			
2	44.1 (Mg)	Mg_2Ni	1.99	1.97
	55.3 (Ni)			
3	45.8 (Mg)	Mg_2Ni	2.01	2.00
	54.6 (Ni)			
4	50.2 (Mg)	Mg_2Ni	1.99	2.00
	49.8 (Ni)			
5	69.1 (Mg)	Mg_2Ni	1.94	2.00
	29.8 (Ni)			
6	94.1 (Mg)	Mg_2Ni	1.84	2.00
	4.8 (Ni)			
7	93.1 (Mg)	Mg_2Ni	1.97	2.00
	6.2 (Ni)			
8	31.7 (Mg)	Mg_2Ni	1.47	1.48
	68.5 (Ni)			

^a From phase diagram.³

Acknowledgment.—The authors wish to thank Mr. Jonathan Hughes for his assistance in the experimental work.

(4) J. F. Stampfer, Jr., C. E. Holley, and J. F. Suttle, *J. Am. Chem. Soc.*, **82**, 3504 (1960).