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Hydriding mechanism of Mg_2Ni in the presence of oxygen impurity in hydrogen

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For the case where oxygen is present as an impurity in hydrogen, a hydriding mechanism is proposed along with hydriding cycling of the Mg_2Ni alloy. The large chemical affinity of magnesium for oxygen leads to the selective oxidation of magnesium and to the segregation of the more noble nickel component. The consequence is a progressive decrease in hydrogen storage capacity of Mg_2Ni along with hydriding cycling. The segregated nickel provides active sites for chemisorption of oxygen and hydrogen. The chemisorbed oxygen accelerates the surface segregation of nickel or can form water vapour with hydrogen, or (least favourably) directly oxidizes nickel. The chemisorbed hydrogen can form water vapour with oxygen, can hydride Mg_2Ni or can reduce the nickel oxide eventually formed. All these reactions are exothermic, causing an increase in temperature during the hydriding process.

1. Introduction

Mg_2Ni is regarded as a powerful candidate for a hydrogen storage material along with FeTi, $LaNi_5$ etc. In this paper possible reactions for the Mg_2Ni–H_2 system are considered from the view point of chemical affinities for the very common case where O_2 is present as an impurity in H_2. A hydriding mechanism is proposed and confirmed with the experimental results and the reported data.

2. Hydriding characteristics of the Mg_2Ni–H_2 system in the presence of O_2 as impurity

Seiler *et al.* [1], after having investigated the surface of Mg_2Ni exposed to O_2 by X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES), reported that a small amount of oxygen induces surface segregation, leading to an overlayer of oxidized magnesium and leaving behind at least some nickel in the metallic state. This can be expressed by the equation

$$O_2 + Mg_2Ni \rightarrow 2\,MgO + Ni \qquad (1)$$

The free energy change ΔG_1 of Reaction 1 is given as

$$\Delta G_1 = \Delta G_1^0 + RT \ln \frac{a_{MgO}^2 a_{Ni}}{P_{O_2} a_{Mg_2Ni}} \qquad (2)$$

where ΔG_1^0 is the standard free energy change of Reaction 1, a is activity and P partial pressure. The standard free energy change ΔG_1^0 of Reaction 1 is given as Equation 5 below by using those of Reaction 3 (ΔG_3^0) and Reaction 4 (ΔG_4^0):

$$O_2 + 2Mg \rightarrow 2MgO \qquad (3)$$

$$2Mg + Ni \rightarrow Mg_2Ni \qquad (4)$$

$$\Delta G_1^0 = \Delta G_3^0 - \Delta G_4^0 \qquad (5)$$

ΔG_3^0 and ΔG_4^0 are given as follows:

$$\Delta G_3^0 = -1\,208\,000 - 24.69\,T \log T + 284.1T \quad \text{(J)}$$

from [2], and

$$\Delta G_4^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_p \mathrm{d}T - T\Delta S_{298}^0 - T\int_{298}^{T} \frac{\Delta C_p}{T}\mathrm{d}t$$

where ΔH^0_{298} and ΔS^0_{298} are the heat of formation of Mg_2Ni ($-51\,900\,J\,mol^{-1}$) and its entropy of formation (nearly zero) [2] respectively, and ΔC_p is the difference of heat capacities between Mg_2Ni and ($2Mg + Ni$): i.e. $\Delta C_p = C_{Mg_2Ni} - (2C_{Mg} + C_{Ni})$. If we apply Kopp's rule [3] that the heat capacity of a solid compound is equal to the sum of the heat capacities of its constituent elements to the calculation of ΔC_p, then $\Delta C_p = 0$. Thus

$$\Delta G_1 = -1\,156\,000 - 24.69T\log T + 284.1T + RT\ln\frac{a^2_{MgO}a_{Ni}}{P_{O_2}a_{Mg_2Ni}} \quad (J) \qquad (6)$$

ΔG_1 characterizes the chemical potential of O_2 in the oxide after segregation of nickel, and $-\Delta G_1$ is the chemical affinity of Mg_2Ni for O_2. This is the driving force for surface segregation of nickel in the presence of O_2 impurity in the hydrogen gas.

The published phase diagram [4] shows that Mg_2Ni is in equilibrium with $MgNi_2$ up to 1034 K. This indicates that the liberated nickel from Reaction 1 can form $MgNi_2$ in our experimental temperature 573 K, as expressed by

$$Mg_2Ni + 3Ni \rightarrow 2MgNi_2 \qquad (7)$$

The free energy change ΔG_7 of Reaction 7 is given by

$$\Delta G_7 = \Delta G^0_7 + RT\ln\frac{a^2_{MgNi_2}}{a^3_{Ni}a_{Mg_2Ni}} \qquad (8)$$

where the standard free energy change of Reaction 7 is $\Delta G^0_7 = -61\,100\,J$, where Kopp's rule for heat capacity is used.

Seiler *et al.* [1] and Schlapbach *et al.* [5] reported that segregated nickel provides active sites for chemisorption of H_2. Our own investigation on the kinetics of the H_2–(Mg_2Ni + 2.7 wt % Ni) system [6] showed that the rate-controlling step in the hydriding process is the chemisorption of H_2, nickel actually providing active sites for chemisorption of H_2.

According to Langmuir [7] a metal filament of tungsten exposed at 1500 K to a mixture of oxygen and hydrogen adsorbs oxygen as if hydrogen were absent; moreover the chemisorbed oxygen prevented the formation of atomic hydrogen. Trapnell [8] reports that O_2 is generally more strongly adsorbed by metals than H_2. These reports suggest that the segregated nickel adsorbs preferentially O_2 to H_2. We therefore consider first the chemisorption of O_2 on the surface of segregated nickel. Brennan *et al.* [9] showed in most metals that each surface atom takes up one atom of oxygen. Therefore the stoichiometric equation for the atomic adsorption of oxygen is generally written as Equation 9 below, where |Ni indicates an active surface site of nickel [10]:

$$2|Ni + O_2 \rightarrow 2|Ni = O \qquad (9)$$

This dissociatively chemisorbed oxygen can directly oxidize Ni (Reaction 10) or Mg_2Ni (Reaction 1) after surface diffusion on nickel, and eventually forms water vapour with H_2 (Reaction 11):

$$2Ni + O_2 \rightarrow 2NiO \qquad (10)$$

where NiO represents conventionally a nickel oxide. According to Gulbransen and Hickman [11], NiO is the stable form of nickel oxide and its appears alone in the oxidation film of nickel in O_2. Also

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (11)$$

From [3], the free energy change of Reaction 10 (ΔG_{10}) and that of Reaction 11 (ΔG_{11}) are given as follows:

$$\Delta G_{10} = -489\,100 + 197.1\,T + RT\ln\frac{a^2_{NiO}}{a^2_{Ni}P_{O_2}} \quad (J) \qquad (12)$$

$$\Delta G_{11} = -492\,900 + 109.6\,T + RT\ln\frac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}} \quad (J) \qquad (13)$$

The activities of all the solid phases are equal to unity, since they are considered as being in their pure standard state. In our experimental conditions

$$T = 573\,K$$
$$P_{H_2} = 1.3 \times 10^5\,Pa$$
$$P_{O_2} = 12\,Pa\ (9\,ppm)$$

and

$$P_{H_2O} = 25\,Pa\ (19\,ppm)$$

the free energy change of Reactions 1, 7, 10 and 11 are

$$\Delta G_1 = -989\,kJ$$

$$\Delta G_7 = -61.1\,\mathrm{kJ}$$

$$\Delta G_{10} = -333\,\mathrm{kJ}$$

$$\Delta G_{11} = -490\,\mathrm{kJ}$$

These negative values indicate that Reactions 1, 7, 10 and 11 are spontaneous processes.

The chemical affinites for Reactions 1, 10 and 11 are in the following order:

$$-\Delta G_1 > -\Delta G_{11} > -\Delta G_{10} \quad (14)$$

This ordering shows that all the oxygen chemisorbed on the nickel surface does not form oxide and that it can accelerate the surface segregation of nickel, but also that it can form water vapour with hydrogen.

The Ellingham diagram ([3], p. 269) shows that nickel oxide can be reduced by H_2 even at room temperture:

$$H_2 + NiO \rightarrow Ni + H_2O \quad (15)$$

The free energy change of Reaction 15 is given as

$$\Delta G_{15} = -1900 - 43.72\,T + RT \ln \frac{a_{Ni} P_{H_2O}}{P_{H_2} a_{NiO}} \quad (\mathrm{J}) \quad (16)$$

In our experimental conditions $\Delta G_{15} = -78.7\,\mathrm{kJ} < 0$.

Equation 14 shows that the oxygen chemisorbed on the nickel surface forms least favourably NiO. Even if it is formed, it will be reduced by H_2 (Equation 15). Secondly the chemisorption of H_2 must be considered. Beeck [12] found that each atom of evaporated nickel films adsorbs one atom of hydrogen. Thus the stoichiometry of hydrogen chemisorption can usually be represented [13] as

$$2|Ni + H_2 \rightarrow 2|Ni - H \quad (17)$$

This chemisorbed hydrogen can hydride Mg_2Ni (Reaction 18) or form water vapour with O_2 (Reaction 11) or reduce nickel oxide (Reaction 15). The hydriding reaction is

$$\tfrac{1}{2}Mg_2Ni + H_2 \rightarrow \tfrac{1}{2}Mg_2NiH_4 \quad (18)$$

The free energy change of Reaction 18 is given by

$$\Delta G_{18} = -64\,400 - 112.2\,T \quad (\mathrm{J}) \quad (19)$$

where Kopp's rule for heat capacity is used and the results of Reilly and Wiswall [14] for the heat of formation of Mg_2NiH_4 and its entropy of formation are employed.

At 573 K, $\Delta G_{18} = -129\,\mathrm{kJ}$. The chemical affinities for Reactions 11, 15 and 18 may be set as follows:

$$-\Delta G_{11} > -\Delta G_{18} > -\Delta G_{15} \quad (20)$$

This indicates that the hydrogen chemisorbed on nickel forms not only Mg_2Ni hydride but also water vapour, and reduces nickel oxide less favourably, from the thermodynamical point of view.

If we consider all heats of reaction or formations (ΔH), they are given as follows from the above equations for the free energy change of reaction:

$$\Delta H_1 = -1156\,\mathrm{kJ}$$

$$\Delta H_7 = -61.1\,\mathrm{kJ}$$

$$\Delta H_{10} = -489.1\,\mathrm{kJ}$$

$$\Delta H_{11} = -492.9\,\mathrm{kJ}$$

$$\Delta H_{15} = -1.9\,\mathrm{kJ}$$

$$\Delta H_{18} = -64.4\,\mathrm{kJ}$$

The heats of chemisorption on nickel by oxygen and hydrogen (ΔH_9 and ΔH_{17} respectively) [15] are given by

$$\Delta H_9 = \sim -420\,\mathrm{kJ\,mol^{-1}\,O_2}$$

$$\Delta H_{17} = \sim -130\,\mathrm{kJ\,mol^{-1}\,H_2}$$

These reactions are all exothermic. This therefore causes an increase in temperature in the course of reaction.

3. A proposal on the hydriding mechanism of Mg_2Ni in the presence of O_2 as impurity

From the above discussions we can propose, as in Fig. 1, the hydriding mechanism of Mg_2Ni in the presence of O_2 and along with hydriding cycles. In Fig. 1, (a), (b) and (c) indicate respectively the reactants, the reactions and the products in the *i*th hydriding cycle. The reactions except the seventh one are written downwards in the order of the magnitude of the chemical affinities ($-\Delta G$) in our experimental conditions. The lines represent the paths of the materials during the reactions. In particular, their widths from the chemisorbed atomic hydrogen and oxygen and from nickel represent the relative magnitudes of their chemical affinities for the other reactants. ΔH_R is the total heat of reactions.

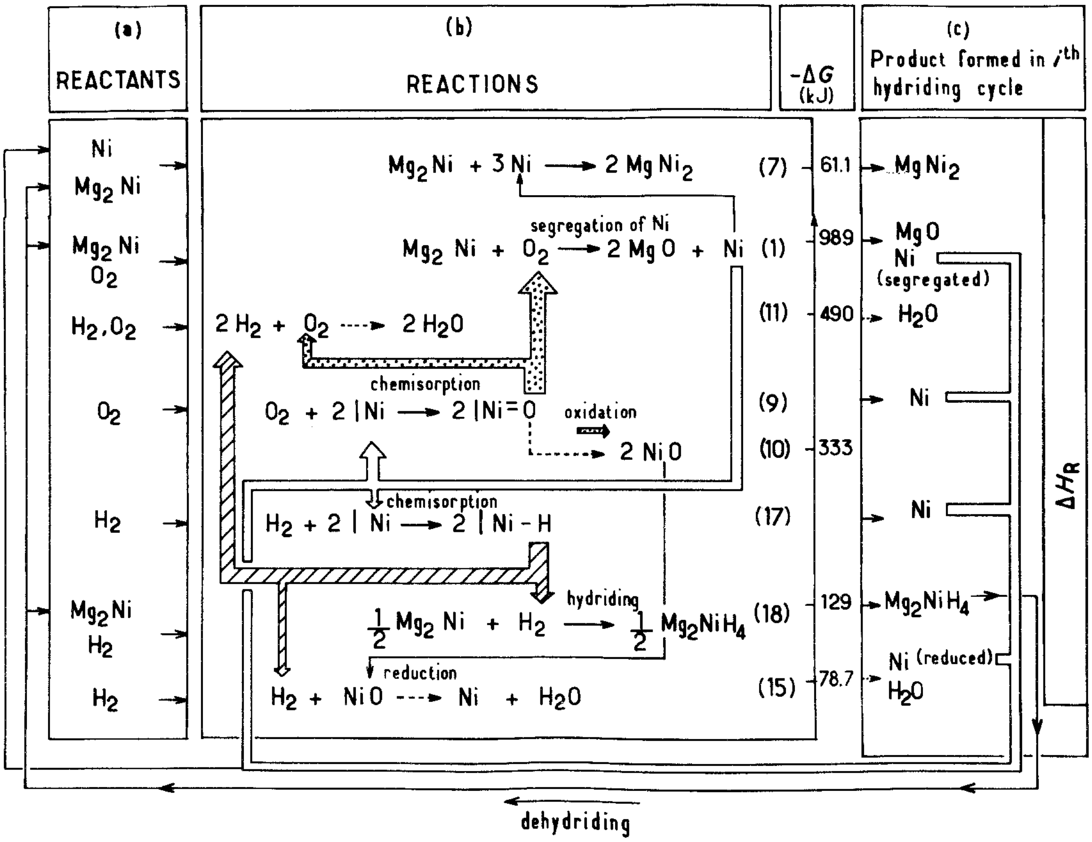

Figure 1 A proposal on the hydriding mechanism of Mg_2Ni in the presence of O_2 as impurity, along with hydriding cycles. For explanation see text.

Now let us consider each reaction:

Reaction 7: nickel segregated in the same hydrogen absorption cycle or formed in the previous sycles forms $MgNi_2$ with Mg_2Ni.

Reaction 1: Chemisorbed atomic oxygen on the surfaces of Mg_2Ni or nickel oxidizes Mg_2Ni to form MgO and nickel (segregated). MgO is too stable to be reduced in our experimental conditions. Segregated nickel provides active sites for chemisorption of O_2 and H_2 in the same hydrogen adsorption cycle or in the following cycles.

Reaction 11: H_2 and impurity O_2 and/or those chemisorbed on the nickel surface combine to form water vapour.

Reactions 9 and 10: O_2 is chemisorbed on the surface of segregated nickel. The chemisorbed oxygen oxidizes Mg_2Ni or combines with H_2 and/or chemisorbed atomic hydrogen to form water vapour, or directly oxidizes nickel (least probably).

Reaction 17: H_2 is chemisorbed on the surface of the segregated nickel. The chemisorbed atomic hydrogen combines with O_2 and/or chemisorbed atomic oxygen to form water vapour, or to hydride Mg_2Ni and/or eventually to reduce the nickel oxide.

Reaction 15: H_2 and/or atomic hydrogen chemisorbed on nickel reduces nickel oxide, eventually formed in the same hydrogen absorption cycle (Reaction 10), resulting in the formation of water vapour.

4. Experimental procedure

The hydrogen used, supplied from *l'Air Liquide*, was purified through a column filled with magnesium chips maintained at 823 K. The O_2 as impurity in the purified hydrogen was determined to be 9 ppm and water vapour 19 ppm by a mass spectrometer. To prepare the intermetallic Mg_2Ni compound, we used magnesium powder (Ventron, −50 mesh, 99.8% purity) and nickel (CERAC, −325 mesh, 99.9% purity). The mixture of magnesium and nickel in the proportions corresponding to composition

$Mg_{2.05}Ni$ was pressed under dynamic vacuum at 0.3 GPa for 2 min. The composition of the mixture was chosen to compensate for the amount of magnesium evaporating during preparation of Mg_2Ni. The mixture was then melted under an argon atmosphere of 0.3 MPa at 1173 K for 1 h in a molybdenum crucible. After grinding and pressing it was homogenized at 973 K for 30 h under argon atmosphere. For the identification of the phases X-ray diffraction and magnetic measurements were used.

The hydrogen storage capacities for hydrogen absorption cycles were measured by the volumetric method. The increase in temperature during the reaction was read by means of a recorder whose thermocouple was located within the bottom wall of the reactor.

5. Results substantiating the model

Fig. 2 shows the variation of magnetization M as a function of magnetic field H. Curve A concerns a sample of Mg_2Ni prepared as above, Curve B Mg_2Ni hydrided at 573 K during 30 h under 1.3 MPa hydrogen pressure. After such a treatment approximately 100% of the sample was hydrided. Curve C designates Mg_2Ni hydrided under the same conditions of temperature and pressure as Curve B for 120 h and then after 25 hydrogen absorption–desorption cycles for 4 h (i.e. four times the hydriding period of treatment of Curve B plus 25 cycles).

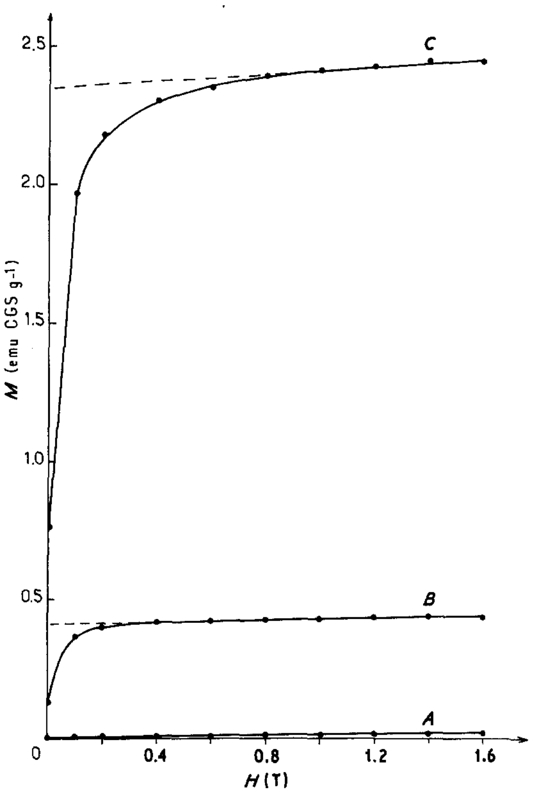

Figure 2 Variation of magnetization with magnetic field for the Mg_2Ni samples with or without hydriding treatment: Curve A, Mg_2Ni as prepared; Curve B, Mg_2Ni hydrided at 573 K under 1.3 MPa H_2 for 30 h; Curve C, Mg_2Ni hydrided at 573 K under 1.3 MPa H_2 for 120 h and after 25 hydriding cycles of 4 h. (1.257×10^{-2} emu ≡ 1 A m^{-1}.)

Curve A shows that the Mg_2Ni sample as prepared indicates practically a paramagnetic behaviour. Curves B and C reveal the segregation of the ferromagnetic nickel (nickel is the only ferromagnetic phase able to form in the Mg–Ni system). The amounts of segregated nickel are ~0.8 and ~4.3 wt% respectively. The comparison of these values shows that segregation of nickel is promoted by hydriding time and hydrogen absorption–desorption cycling.

Fig. 3 gives the X-ray powder diffraction diagrams (a) for the Mg_2Ni sample as prepared, and (b) for the sample after 94 hydrogen absorption–desorption cycles at 573 K under 0.7 MPa H_2. Each cycle took at least 1 h. Figs. 3a and b allow one to detect $MgNi_2$ and MgO. In Fig. 3b their amount is higher than in Fig. 3a, showing that hydrogen absorption–desorption cycling increases their formation.

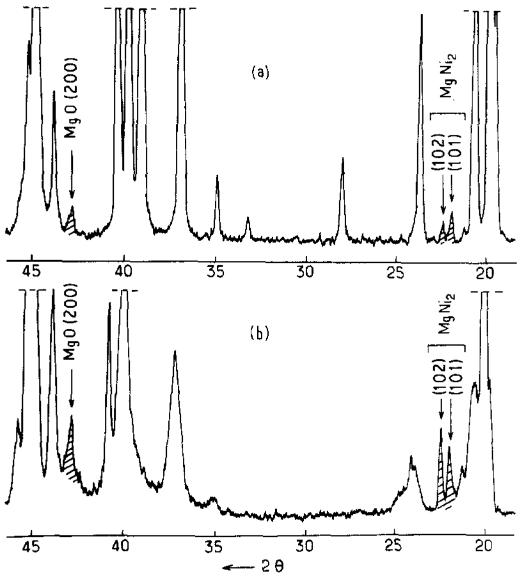

Figure 3 X-ray diffraction patterns: (a) for Mg_2Ni as prepared, (b) for Mg_2Ni after 94 hydriding cycles.

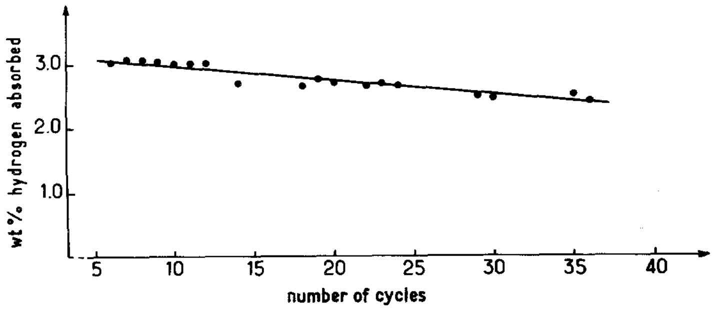

Figure 4 Percentage H_2 absorbed under 0.7 MPa H_2 during 1 h as a function of number of cycles after five activation cycles at 573 K.

These results (Figs. 2 and 3) indicate clearly that Mg_2Ni is oxidized by O_2 present as an impurity to form magnesium oxide and segregated nickel. The chemical affinity of magnesium for O_2 is actually much higher than that of nickel (in our experimental condition 1063 kJ; compare this with $-\Delta G_{10}$). This may be considered as the driving force for bonding magnesium to the oxygen present, nickel being left in the metallic state (Reaction 1). The oxygen chemisorbed on the segregated nickel (Reaction 9) oxidizes Mg_2Ni preferentially from the viewpoint of chemical affinity. Thus we can consider that segregated nickel accelerates the oxidation of Mg_2Ni by chemisorption of oxygen (self-catalytic process). As concerns the formation of $MgNi_2$, the annealing effect (at 573 K under our experimental conditions) is considered to play an important role. All the segregated nickel does not form $MgNi_2$ because of the arrangement of nickel and Mg_2Ni phases and the experimental conditions.

Benton and Emmett [16] showed that water vapour was formed after passing the mixture of hydrogen and oxygen on nickel above 373 K. Donelly [17] also reported that nickel plays the role of a catalyst for the formation of water vapour. Under our experimental conditions water vapour can be formed and the segregated nickel can act as a catalyst for this reaction, but a dotted arrow is used for this reaction since we have no evidence.

The chemisorbed hydrogen (Reaction 17) can either form water vapour with oxygen or hydride Mg_2Ni (Reaction 18) or even reduce nickel oxide. The temperature at which the reduction of nickel oxide by hydrogen begins is about 390 K according to Gallo [18], and about 500 K for the investigation of Saito [19]. It follows that in our experimental conditions the NiO eventually formed can be reduced (Reaction 15)

Fig. 4 shows the percentage of H_2 absorbed during 1 h under 0.7 MPa H_2 as a function of the number of hydriding cycles after five previous activation cycles at 573 K. The absorption of H_2 by the sample decreases as the number of hydriding cycles increases. This result shows that Mg_2Ni is continuously oxidized to form MgO and nickel, resulting in the diminution of Mg_2Ni phase to absorb hydrogen.

Fig. 5 shows the increase in temperature ΔT during the hydriding reaction of Mg_2Ni of a 0.6 g sample under 0.7 MPa H_2 at 573 K. This

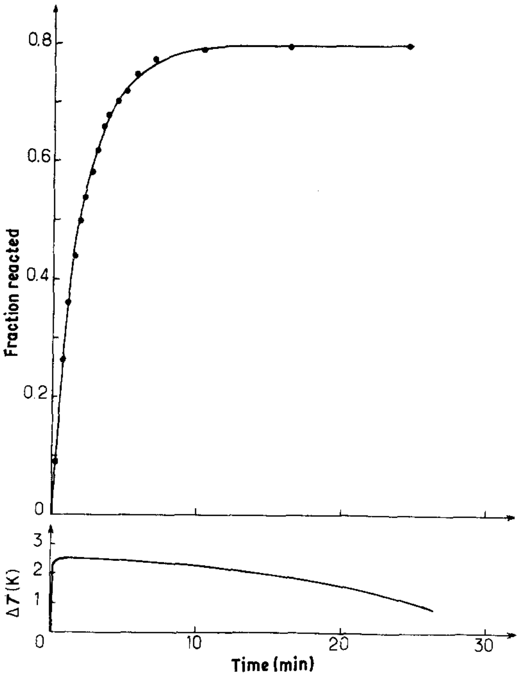

Figure 5 Increase in temperature during hydriding reaction of Mg_2Ni of a 0.6 g sample under 0.7 MPa H_2 at 573 K.

results from the total exothermic heat of reaction ΔH_R. Its main part is the heat of chemisorption and the heat of formation of Mg_2Ni hydride, as the amount of O_2 present is very small (9 ppm) in comparison with that of H_2.

We consider that a similar mechanism can be applied to the hydriding of FeTi, $LaNi_5$, $ErFe_2$ etc. which show similar hydriding phenomena. Each alloy contains a transition element and another readily oxidizable element, showing surface segregation of the transition element in the presence of oxygen impurity in hydrogen.

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