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ON THE RELATION BETWEEN THE THERMAL STABILITY OF MgH_2 AND HYDRIDING KINETICS

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ABSTRACT

As a hydrogen-absorbing material, magnesium metal is considered to be the most promising because of its large absorbing capacity(c.a. 7,6 wt%). The kinetic data are usually obtained by repeated cycling of hydriding and dehydriding[1]. We have first observed that the reactivity of partly hydrided magnesium can be modified by treating at P_{eq}. We demonstrated that dehydriding kinetics are so sensitive to the material preparation that it is questionable whether any of the rate constants obtained by repeating cycling have a fundamental significance.

EXPERIMENTAL

The magnesium powder was manufactured by an atomizing process whereby molten metal is sprayed into an inert atmosphere. This method creates particles of an almost spheroidal shape. The starting powder was separated by specially constructed device into fractions of different grain sizes. The kinetic data were obtained for a fraction of the particle diameter of 5-10µm.

The hydrogen absorption and desorption were carried out by the combination of a manometric and volumetric methods [e.g.2]. The pressures were measured by means of piezoresistive transducers (Sapphire) with an overall precision better than 0.25% (0-25 bar). The temperature was measured with a thermocouple introduced directly into the sample.

RESULTS AND DISCUSSIONS

We used the dehydriding kinetics as a measure of the reactivity of Mg-H system. Fig.1 demonstrates the dehydriding rates of the magnesium hydrided to the different (reacted fractions) with the same driving force (overpressure and temperature). The 1,2 and 3 curves can be followed by the equation:

$$1 - (1 - \alpha)^{1/2} = kt \qquad (1)$$

where α is number of H_2 moles desorbed during t min/ number of H_2 moles absorbed by the sample during its previous hydriding. Note that curves 1 and 2 are the parts of the curve 3.

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On the curve 4 there is a small acceleration period while the maximal rate is nearly the same as for 3. Dehydriding of the samples hydrided up to F = 70% (F is caculated on the assumption that 100% of the sample is hydrided into the composition of MgH_2) is presented by the curves 5 and 6 followed by the Arrami-Erofeev equation:

$$-\ln (1 - \alpha)^{1/2} = kt$$

The curves 5 and 6 can be transformed to the curve 6 and vice versa by simple changing the ordinate scale. We emphasized that the maximal rates ofgas elimination V_{des} are rather low for 5 and 6 curves than that for the curves 1-4. Changing a driving force of the reaction (e.g. overpressure P/P_{eq}) one can change the reaction time t_F necessary for hydriding up to chosen value of F.

In fig.2. the dependence of the initial hydrogen desorbtion rate V_{des} is plotted against the time of previous hydriding reaction t_F = 0.4. Desorbtion always began with maximal rate and was described by the equation (1).

Whatever were the values of t_F=0.4 one can drastically decrease the values of the V_{des} by treating a sample at P_{eq} (fig.3).

The experimental data obtained demonstrate a complex behaviour of the Mg-H system, which can be explained by the following speculations.

The formation of a chemisorbed hydrogen layer on the sample surface seems to be the first important step of the hydriding process. The former hydriding is developed due to nucleation and growth mechanism rather than a coating hydride layer growing. Almost the same model was first proposed by Benard[3] for the oxidation of metals.

Within this model a driving force of the reaction (overpressure for hydriding or e.g. supersaturation for crystallization from a solution) have the fundamental significance. The same values of F can be realized by changing the size and number of MgH_2 nuclei if changing the driving force (P/P_{eq}). We supposed that V_{des} is determined by two factors: nucleation in MgH_2 – N_{MgH_2} and/or decomposition on the phase boundary Mg-MgH_2-S_{MgH_2}. Supposing N_{MgH_2} to be constant at constant driving force, V_{des} might depend mainly on the changing of S_{MgH_2} with changing of size and number of MgH_2 nuclei. If to stop the hydriding when nuclei have not been overlops yet no nucleation of N_{MgH_2} is needed for the desorbtion and V_{des} is large (fig.1). The decreasing of V_{des} by treating a sample at P_{eq} seems to be accounted for the recrystallization of MgH_2 nuclei when S decreases. The same type of recrystallization takes place in solid-liquid solution systems under equilibrium when small crystals dissolved while large grew. Indeed, a long time treating of the sample at P_{eq} (e.a. 3 days) resulted in sigmoid like kinetical curves of the desorbtion and very low V_{des}.

CONCLUSIONS

When studying the thermal decomposition of magnesium hydride one should take into account that its reactivity depends upon both F and driving force applied during hydriding. The aging of the samples during repeated cycling is also important.

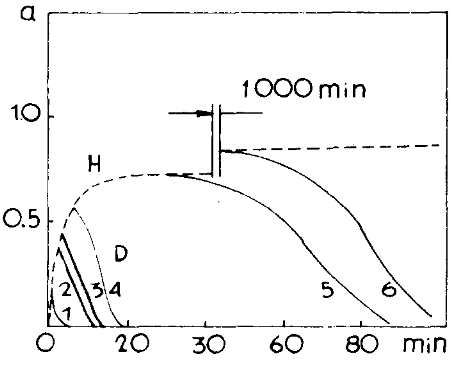

Fig.1.

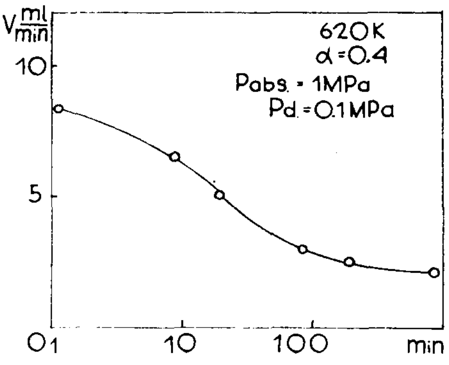

Fig.3.

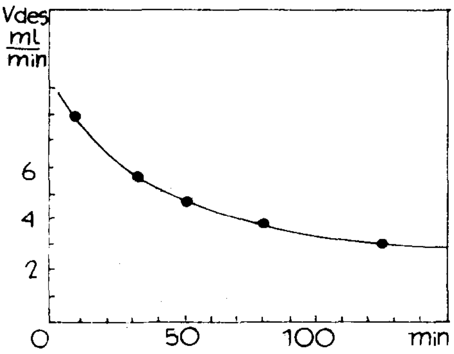

Fig.2.

REFERENCES

1 A.S. Pedersen, J. Kjoller, B. Larsen, B. Vigeholm, Int. J. Hydrogen Energy, 8,(1983), 205

2 A.S. Pedersen, J. Kjoller, B. Larsen, B. Vigeholm, J.A. Jensen, Int. J. Hydrogen Energy, 9, (1984), 799

3 J. Benard, F. Gronlund, J. Oudar, M. Duret, Z. Elektrochem., 63, (1959), 799