Hydrogen absorption of LaNi$_5$ powders precovered with O$_2$, CO, H$_2$S, CO$_2$ or N$_2$

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Abstract

LaNi$_5$ powder samples were first exposed to contamination gases such as O$_2$, CO, H$_2$S, CO$_2$ or N$_2$ and then loaded with pure hydrogen gas. The coverage needed for poisoning was measured and the absorption kinetics of poisoned and unpoisoned samples is described.

Keywords: Kinetics; Poisoning; Contamination; LaNi$_5$

1. Introduction

One of the major problems of hydrogen storage alloys is their susceptibility to surface contamination by reactive gases [1–4]. Residual impurity gases adsorbed at the surface of the storage alloy can drastically decrease the absorption and desorption rates of hydrogen by impeding the dissociation of the H$_2$ molecules. Even low impurity concentrations in the hydrogen gas can cause problems in applications if storage alloys are subjected to repeated loading and unloading cycles.

Investigations on the poisoning behavior of impurity gases normally examine the effect of additives in the hydrogen gas on the absorption rate and on the loading capacity of storage alloys [2–4]. The results are informative for practical applications but they yield no direct correlation between surface coverage of the sample and reduction of the reaction rate. An analysis of the reaction kinetics is difficult since the surface conditions change during the absorption process. In the present work a different type of experiment is performed: The powder samples are first exposed to a known quantity of contamination gas and then loaded with pure hydrogen [5]. This provides a direct interrelation between the amount of contamination gas in the system and the hydrogen absorption rate.

2. Experimental

The activation procedure, loading and poisoning of the LaNi$_5$ powder samples were performed in a Sieverts' apparatus equipped with a diffusion pump with which a base pressure of 10^{-5} mbar was attained. The samples were exposed to an initial hydrogen pressure of 11.5 bar at room temperature and the final pressure in the reactor after loading was 9.5 bar. Only small quantities of LaNi$_5$ powder (0.5 g) were taken in order to minimize the heat that must be transferred to the reactor wall. No heat buffer was used to prevent errors in the determination of the coverage of the LaNi$_5$ sample with contamination gas. The hydrogen was of 6.0 purity (99.9999%) and CO, O$_2$, H$_2$S, N$_2$, and CO$_2$ were taken as contamination gases.

Each run was performed by the following procedure: First a new powder sample was activated and then exposed to a defined amount of contamination gas for 10 min. After this poisoning treatment the reactor was evacuated again and the sample loaded with pure hydrogen. The reaction rate was determined from the pressure decrease in the reactor. The surface area of the powder sample was obtained by granulometric measurements. Since the amount of contamination gas present in the receiver and the sample surface was known, the contamination gas exposure can be given in units of monolayer equivalent (1 ML $= 10^{19}$ molecules m^{-2}).

A new sample was taken for each run with different contamination gas precoverage. Therefore, the activation process must be well defined in order to get comparable initial conditions. A solid LaNi$_5$ sample of about 0.5 g was degassed at 500 K and then cycled with pure hydrogen gas. It breaks into small powder particles with a mean radius of 11 μm. After 13 cycles a stable absorption behavior is attained with a 50% loading time of 5 s which is about the same as observed in measurements performed with a heat

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buffer [6]. Further cycling of the powder samples yields only small changes of the mean particle size [5,7]. The surface area of the powder sample was determined to be $0.2 \ m^2 \ g^{-1}$ which is in agreement with data of other authors [8].

3. Results and discussion

In Fig. 1 the relative reaction rate v/v_0 of hydrogen with $LaNi_5$ powder is shown as a function of the contamination gas exposure. The initial reaction rate v for the samples is normalized to the value of the initial reaction rate v_0 of uncontaminated $LaNi_5$ samples. The exposure of the $LaNi_5$ powder to contamination gas is given in units monolayer equivalents with respect to the $LaNi_5$ powder surface (ML). This does not mean that the whole amount must have been absorbed. N_2, CO_2, H_2S and CO are known to form only one or not much more than one monolayer of adsorbate on metal surfaces [9]. The curves in Fig. 1 show that the hydrogen absorption rate is changed differently after precoverage with different gases. Precoverage with N_2 does not affect the hydrogen absorption rate at all. For all other gases the initial reaction rate is reduced by a factor of two to ten when the sample has been exposed to about one ML of contamination gas. For CO and H_2S the initial reaction rate is reduced drastically by factors higher than 10^5 if the sample is exposed to two or three ML. The reaction rate for samples exposed to CO_2 remains constant at a factor of 0.04 for exposures exceeding one ML. Oxygen shows a complex behavior. After 4 ML precoverage a plateau is reached and further decrease of the reaction rate is observed only after about 7 ML O_2. It should be noted that the absorption rate for hydrogen is not increasing again with increasing amounts of absorbed O_2 in this type of experiment as it had been reported for experiments with O_2/H_2 gas mixtures [5,10,11].

The reacted fraction $F=c/c_{max}$ of the sample is shown in Fig. 2 as a function of the reaction time in a double logarithmic plot for different precoverages with CO. The

Fig. 2. Reacted fraction $F=c/c_{max}$ versus reaction time for various values of CO preexposure. The exponent n of the time law $F\sim t^n$ is given for $F=0.3$.

exponent n in the time law $F\sim t^n$ decreases with increasing hydrogen concentration F for the unpoisoned sample. This behavior is characteristic for a diffusion controlled reaction with spherical geometry. For a diffusion process with a planar geometry an exponent $n=0.5$ is expected [5,13] and with spherical geometry n becomes smaller with increasing F [12,13]. For $F\leq0.3$ the diffusion process can be considered to be planar. The value of $n=0.7$ for $F=0.3$ given in Fig. 2 for the unpoisoned sample shows that even for clean samples the reaction is not controlled only by diffusion. With increasing CO preexposure the exponent n of the time law approaches values close to one and the reaction rate becomes independent of the reacted fraction up to F values of 0.6 or higher (not shown in Fig. 2). This indicates that a surface controlled reaction mechanism is active. If the amount of CO is increased further the exponent exceeds by far the value of one. This behavior is attributed to cracking or spalling of the surface layer or further fragmentation of the $LaNi_5$ powder particles with generation of new unpoisoned surface areas. H_2S poisoning shows similar features as CO poisoning.

In Fig. 3 the reaction rate for oxygen precovered samples is shown. In contrast to CO experiments the exponent approaches a value close to one even for larger
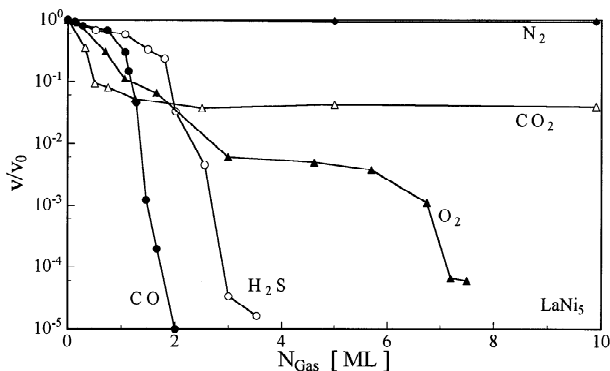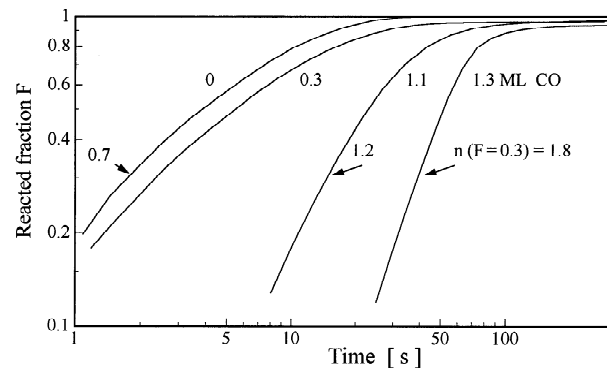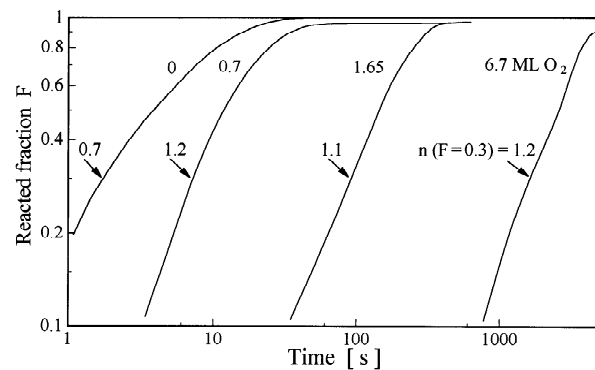

Fig. 1. Initial rate of hydrogen absorption by $LaNi_5$ samples as a function of the preexposure to contamination gases.

Fig. 3. Reacted fraction $F=c/c_{max}$ versus reaction time for various amounts of O_2 preexposure. The exponent n of the time law $F\sim t^n$ is given for $F=0.3$.
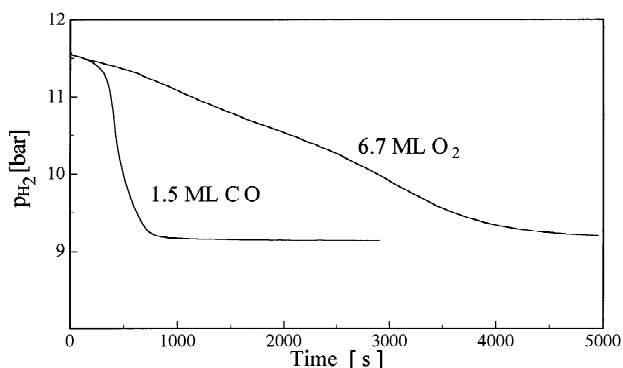
Fig. 4. Hydrogen pressure in the reactor as a function of the reaction time for poisoned LaNi$_5$ samples.

Fig. 5. Initial reaction rate versus number of cycles for experiments with H$_2$/CO gas mixtures.

exposures. This behavior is explained by a plot of the pressure drop in the reactor versus reaction time for strongly poisoned samples (Fig. 4). In the beginning of the experiments a solid solution is formed with a small volume change of the powder particles. The reaction rates are comparable for both gases in this region. As soon as hydride is formed the volume of the powder particle is increased, surface coatings on the individual particles are cracked and new unpoisoned surface areas are created. In this region the reaction rate of the samples precovered with CO increases drastically whereas for O$_2$ precovered samples the reaction rate remains more or less constant. This demonstrates that with CO precovered samples the freshly generated surface areas remain unpoisoned but with O$_2$ precovered samples the new unpoisoned surfaces are poisoned again at once. Since no O$_2$ molecules are present in the gas phase the oxygen must come from the surface. On LaNi$_5$ particles the oxide film is thicker than one ML and the mobility of the oxygen atoms must be high enough to move the latter to unpoisoned parts of the surface. This effect cannot work with CO chemisorption layers since they are only one ML thick [9]. With the CO precovered sample shown in Fig. 4 an additional experiment was performed: The hydrided sample was degassed, then hydrided again without a preceding activation procedure, and finally poisoned with CO. The reaction rate in the second run was almost as high as the reaction rate of the initially activated sample. This time, however, much less than one ML CO exposure poisons the reaction again completely. This observation supports the finding that CO molecules are tightly fixed to the surface and that the reaction rate of hydrogen with CO poisoned LaNi$_5$ samples is controlled by the uncovered surface areas available.

LaNi$_5$ samples precovered with CO$_2$ can be used for studies on the pressure dependence of the reaction rate since they have a constant initial reaction rate v/v_0 of 0.04 for precoverages higher than 3 ML (Fig. 1). The experiments performed here are not isobaric. For a diffusion controlled reaction a pressure dependency of the rate law $v \sim p^{0.44}$ is predicted and for a surface controlled reaction $v \sim p^{0.94}$ [5]. The experimental value of the exponent was
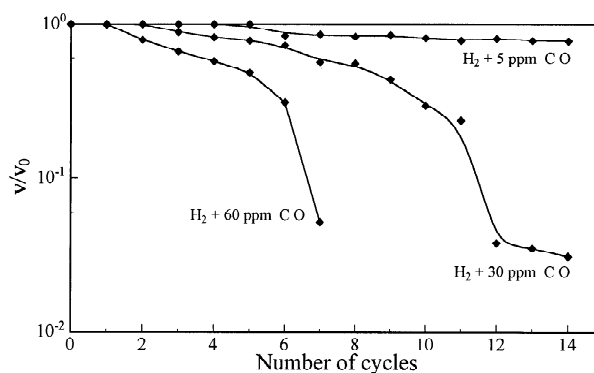
$v \sim p^{0.8}$ for uncontaminated samples and $v \sim p^{1.1}$ for CO$_2$ precovered samples. This demonstrates again that uncontaminated samples are in a transition region where the reaction is controlled by both diffusion and surface processes.

In Fig. 5 results of experiments with a H$_2$/CO gas mixture are shown. The normalized initial reaction rate v/v_0 is plotted as a function of the number of cycles for three different H$_2$/CO ratios. The results agree with measurements of precovered samples. The reaction rate decreases strongly after the powder had been exposed to two or three ML of CO. However, the kinetics is totally different for the two types of experiment. In Fig. 6 the reacted fraction as a function of time is shown for a H$_2$/30 ppm CO gas mixture. A kink in the absorption curves after about 20 s reaction time separates the reaction mechanism into two regimes. The reduced reaction rate is caused by poisoning of the clean surface areas which have been generated by cracks on the particle surface during the preceding degassing treatment.

4. Conclusions

The time law observed for hydrogen absorption by uncontaminated LaNi$_5$ samples indicates that the reaction
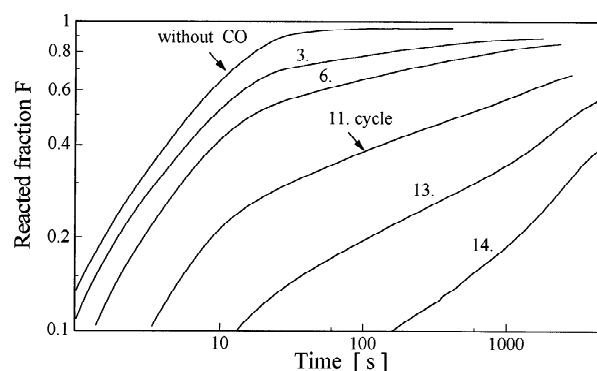

Fig. 6. Reacted fraction F versus reaction time after different cycles with a H$_2$/30 ppm CO gas mixture.

mechanism is controlled by both hydrogen diffusion in the bulk and surface processes. With increasing contamination of the samples the exponent n in the time law $F \sim t^n$ increases and after the ratio v/v_0 has been decreased below 0.1, n approaches a value close to one. The reaction is then surface controlled. Values of n larger than one indicate that spalling of surface layers or cracking of the LaNi$_5$ particles has occurred and unpoisoned surface areas are produced during the absorption process. Comparison of measurements with precovered samples in pure hydrogen and of samples exposed to gas mixtures demonstrate, that a quantitative analysis of the kinetics is much more conclusive for experiments performed with precovered samples since the amount of adsorbed contamination gas is constant in the course of an absorption run.

Acknowledgments

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