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Effect of hydrogen pressure and temperature on the reaction kinetics between Fe-doped Mg and hydrogen gas

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ABSTRACT

The effect of hydrogen pressure and of reaction temperature on the phase transformation from Mg to MgH_2 by exposure of Fe doped metallic Mg to hydrogen gas has been studied with the purpose of evaluating the importance of operative parameters on the hydrogen storage characteristics of this system. Two temperatures have been investigated and, for each temperature, two values of the hydrogen gas pressure. The gas pressure has been adjusted in order to induce the same thermodynamic driving force in samples processed at different temperatures, with the aim of separating the effect of temperature from the one of gas pressure. Experimental results show that the reaction mechanism is independent from the value of the operative parameters which, instead, influence strongly the absolute value of the kinetics constant. Sample microstructure during phase transformation is affected in a major way by the reaction temperature, with the gas pressure playing a minor role.

1. Introduction

Hydrogen is expected to be a valid alternative to the traditional energy carriers, even in a near future. In fact, it can be produced from a variety of sources and it is extremely environmentally benign since water is the only exhaust product when energy is derived from the reaction with oxygen. While hydrogen production is already technologically feasible, the storage and distribution require further development to overcome technological limits and to reduce the connected costs in order to support a wide diffusion of this energy carrier. Compressed gas or cryogenic liquid delivery does not satisfy most of the needs of end users, so that, among others, solid-state storage in reversible or chemical hydrides is explored extensively. In particular, the Mg based hydrides represent promising candidates for hydrogen storage in both stationary and mobile application owing to the high and reversible hydrogen capacity (7.6 wt%). The main problems are related to the high temperature required for hydrogen release and to the slow rate of hydrogen desorption. Important kinetics acceleration has been obtained by intensive plastic deformation and catalyst introduction, generally performed by ball milling; in this way the reaction rate limiting steps present in the pristine material can be overcome [1,2]. Generally speaking about the acceleration of reaction kinetics, the determination of the rate-determining step is the most important key in order to define a strategy to improve the material performances [3,4].

The integration of the classical kinetics analysis performed both during the hydrogen absorption and desorption reactions with microstructural observations based on low voltage scanning electron microscopy has been shown to be able to provide a more detailed information where also the role of localized features like free surface, catalyst particles and defects [5,6] is elucidated. The spatial distribution of the different phases in the material is in fact able to provide important information on the phase transformation, like nucleation site and nucleation rate which are often difficult to obtain by indirect methods.

In order to understand the role of the thermodynamic parameters on the features of reaction of Mg with hydrogen gas, the phase transformation from Mg to MgH_2, in samples containing 5 wt% of Fe, has been studied in different conditions by changing the temperature and the hydrogen gas pressure. In particular the reaction has been studied at two different temperatures and for two values of the thermodynamic driving force. In order to get separated information on the effect of the temperature and of the driving force, experiments at different temperatures have been carried out by adjusting the corresponding hydrogen gas pressure in order to keep constant the thermodynamic driving force of the reaction.

2. Experimental details

The starting powder is composed of 95 wt% MgH_2 (Th. Goldschmidt, 60 μm particle size, 5 wt% of Mg impurity) and 5 wt% Fe (Noah Chemical, 200 mesh, 99.95 wt% purity). The powder was milled for 10 h under 6.0 bar of Argon in a Spex 8000 mixer-

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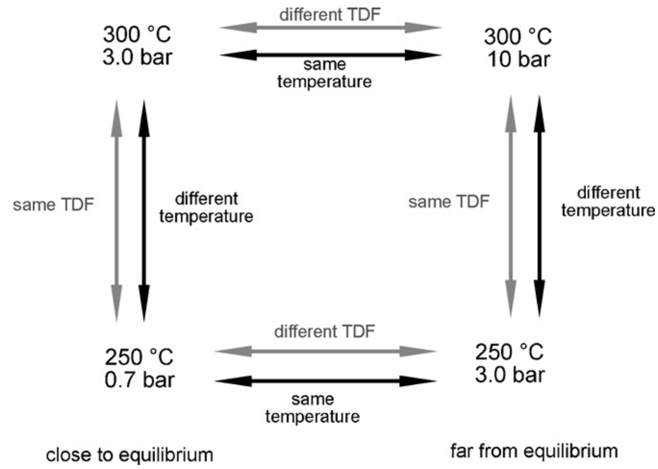

Fig. 1. Experimental scheme, TDF is thermodynamic driving force.

mill with hardened steel spheres with a ball to powder ratio of 10:1. After milling the powder was completely dehydrogenated at 300 °C at 0.2 bar H_2 in a Sieverts' volumetric apparatus (Hydrogen Sorption Analyzer by Cantil srl); the resulting powder was so composed of pure metallic Mg with dispersed Fe particles. This material represents, for this set of experiments, the pristine materials whose reaction with hydrogen gas has been studied at different temperatures and gas pressures.

Four reaction conditions have been studied as schematically described in Fig. 1. In particular the temperatures have been set at 250 °C and 300 °C and, at each temperature, two different gas pressures have been tested. The values of the gas pressure have been selected, according to the formulation of Rudman [7], in order to set up two experimental conditions where the reaction is driven by the same thermodynamic driving force even if the experiment occurs at different temperature. The two different conditions have been chosen in order to evidence the effect of the thermodynamic driving force on the features of the reaction. In particular we have set the gas pressure quite close to the equilibrium condition in a first experiment and relatively far from the equilibrium in the second. In this way a slow reaction is expected in the first case and a faster reaction in the second.

The reaction kinetics has been measured by the volumetric method while metallographic analysis was performed on partially transformed material where about 15 wt% of MgH_2 was present.

In order to prepare cross-sectional samples exposing the microstructure of the powder bulk, the powder was embedded in Al according to a standard protocol already described [5]. A ZEISS EVO MA15 Scanning Electron Microscope was operated at 1 kV to acquire secondary electron (SE) images while backscattered electron (BSE) images were taken at 20 kV.

The stereological analysis of the SEM images was performed by the ImageJ program [8].

3. Results and discussion

The aim of this study is to explore the effect of temperature and hydrogen gas pressure on the features of the reaction of metallic Mg powder during the phase transformation to MgH_2.

We have used a method based on the combined analysis of kinetics curves and metallographic study of partially transformed samples, which has been already used for the unambiguous determination of the reaction rate-limiting step during the hydrogenation reaction of Mg catalyzed with a dispersion of Fe particles [9].

The experimental results concerning the reaction kinetics are reported in Fig. 2 where the material transformed fraction is plotted versus the reaction time. Experimental data are reported as dotted lines while the results of the fitting according to Johnson–Mehl–Avrami (JMA) [10–12] are superimposed as a full line. This model has been preferred to the contracting volume [13,14] since it is best fitting the experimental data in all the experiments, indicating that in our experimental conditions, the nucleation and growth mechanism is at the basis of the phase transformation.

The Avrami exponent, which is left as a free parameter in the fitting procedure, has been determined from a least square analysis,

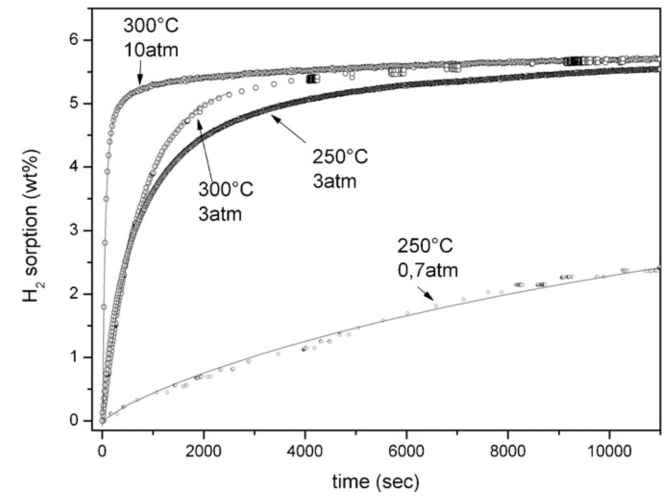

Fig. 2. Hydrogenation kinetic curves in dotted line and respective fitting in solid line.

and it has been found to range from 0.95 to 1.02. These values, very close to $n = 1$, are the marker of the rate limiting step of the reaction, which, considering the constant value resulting from the experiments appears to be the same for all the explored experimental conditions.

Considering that $n = a + bc$, where a ($a \geq 0$) is related to the nucleation rate ($a = 0$ for instant nucleation; $0 < a < 1$ for decreasing nucleation rate; $a = 1$ for constant nucleation rate; $a > 1$ for increasing nucleation rate), b is related to the growth dimensionality ($b = 1$, 2 and 3) and c indicates diffusion-controlled ($c = 0.5$) or interface-controlled ($c = 1$) growth [15], a value of $n = 1$ can be compatible with both interface controlled one-dimensional growth and two-dimensional diffusion controlled growth, while it clearly indicates that nucleation occurs instantaneously so that the phase transformation is expected to proceed at constant density of MgH_2 precipitates per unit material volume.

We have already shown that this last feature find support from the experimental since a constant density of MgH_2 precipitates has been measured at different stages of the phase transformation [9,16].

The kinetics factors k, also determined by the best fitting procedure are reported in Table 1.

It is possible to notice that k increases both by increasing the temperature and thermodynamic driving force. In particular, when samples are reacting with a comparable value of the driving force, the temperature is playing a critical role in the reaction kinetics for both values of the driving force.

The microstructure of the partially reacted samples is reported in Fig. 3, where Mg and MgH_2 phases are clearly evidenced by a different contrast, the darker areas in the SEM images corresponding to the latter. SEM observations show that, in all specimens, the nucleation of MgH_2 phase occurs in the material bulk, often where the Fe particles are, evidencing the role of the catalyst particles in supporting the nucleation step, as already reported [17]. Further

Table 1
Avrami coefficient and absorption rate calculated by application of JMA model to the absorption kinetics curves reported in Fig. 2.

300 °C/3.0 bar $n = 1$ $k = 1.3 \times 10^{-3}$ wt% s^{-1}	250 °C/0.7 bar $n = 1$ $k = 5.9 \times 10^{-5}$ wt% s^{-1}
300 °C/10 bar $n = 1$ $k = 1.1 \times 10^{-2}$ wt% s^{-1}	250 °C/3.0 bar $n = 1$ $k = 6.5 \times 10^{-4}$ wt% s^{-1}