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THE H-SORPTION BEHAVIOUR OF BALL-MILLED MgH_2 – 5 MOL.% FeF_3 STUDIED BY IN-SITU SMALL ANGLE NEUTRON SCATTERING

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Abstract. We report on ball-milled MgH_2 composite powder containing 5 mol.% FeF_3, which were characterized by Small Angle Neutron Scattering (SANS) measurements carried out during *in-situ* H_2 absorption/desorption cycles. In the room temperature SANS curves for the as-milled powder, a power-law regime can be recognized for 0.02 Å^{-1} $< q < 0.15$ Å^{-1}. Within this range, a linear fit yields a power-law scattering exponent α of about 2.4, indicating that the scattering entities can be associated with mass fractals with fractal dimension $D \approx 2.4$. Scanning Electron Microscopy confirms the presence of powder particle aggregates and self-similarity features, which are characteristic of fractal structures. Upon cycling, a power-law regime is again observed for 0.02 Å^{-1} $< q <$ 0.15 Å^{-1}, α exhibiting values of about 3.5 and 4 after desorption and absorption, respectively. The former value can be related to surface fractals with fractal dimension D of about 2.5, whereas for $\alpha = 4$ Porod's law is satisfied. This suggests the development, upon cycling, of a pore structure when Mg forms and its disappearance when MgH_2 forms.

1. INTRODUCTION

Magnesium hydride is considered as one of the most attractive candidate materials for hydrogen storage, due to its high gravimetric capacity and low cost. However, any practical application has been severely limited by a slow absorption and desorption kinetics [1]. This drawback was addressed by many investigations, which focused on improving the reaction kinetics by both tailoring the MgH_2 microstructure and adding a proper catalyst. For instance, it has been shown [2] that processing MgH_2 by high-energy ball milling techniques is beneficial, as fresh and clean surfaces are created at each impact and different kind of crystalline defects are introduced in the lattice. At the same time, MgH_2 grains are reduced to nanometer scale, the resulting path for hydrogen bulk diffusion within the material being significantly shortened. Ball milling has been also used for producing nano-composites in which MgH_2 is mixed with transition metals (e.g. V, Ti, Fe, and Ni) [3], transition metal oxides, e.g. Nb_2O_5 or V_2O_5 [4] or transition metal fluorides such as FeF_3 [5,6].

In this work, ball-milled MgH_2 composite powders containing 5 mol.% FeF_3 were investigated during H_2 absorption/desorption cycles by in-situ Small Angle Neutron Scattering (SANS). The presence of fractal structures is suggested, as positive

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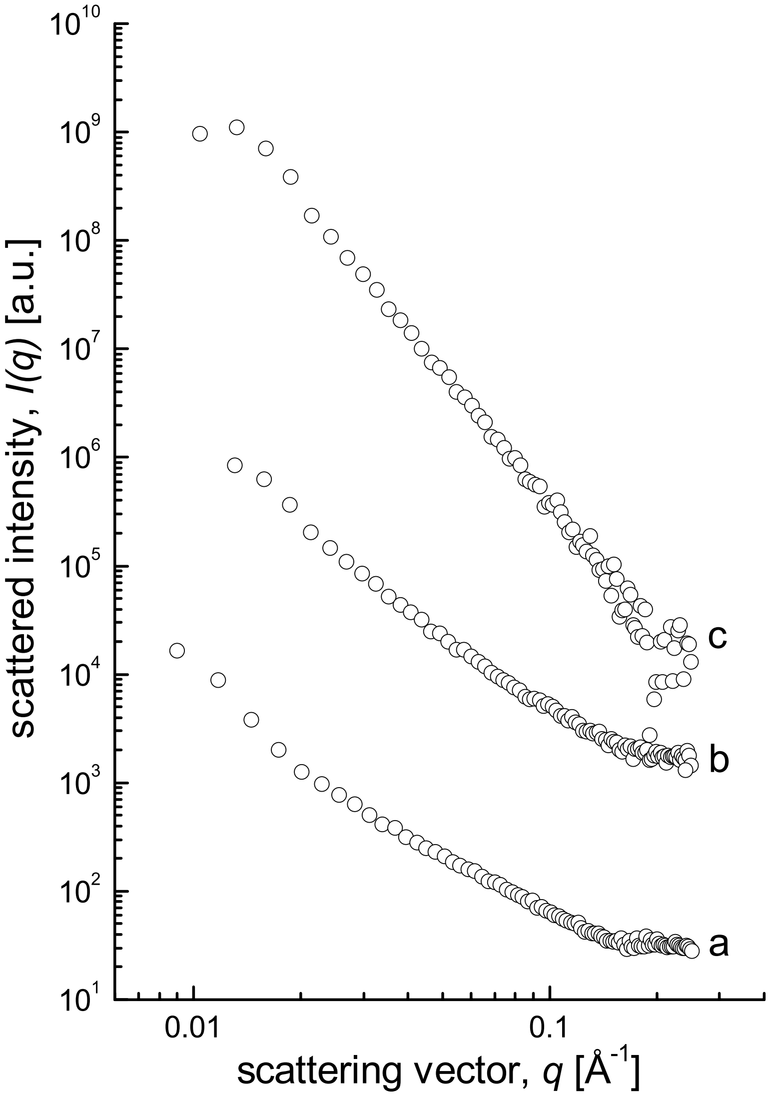

Fig. 1. SANS curves for MgH_2 + 5 mol.% FeF_3 composite powders in the as-milled state (a,b) and after one desorption/absorption cycle (c). The curves have been translated vertically with respect to each other for better visualization. A linear fit in the range 0.02 Å^{-1} < q < 0.15 Å^{-1} resulted in the following power-law scattering exponent α: 2.47 (a), 2.28 (b), and 4.08 (c).

deviations from Porod's law are observed for 0.02 Å^{-1} < q < 0.15 Å^{-1}, q being the scattering vector.

2. EXPERIMENTAL

Ball milling was performed in a Fritsch Pulverizette P0 using hardened steel balls and vials. MgH_2 (Sigma-Aldrich, 90% purity, the rest being magnesium) and FeF_3 anhydrous (Alfa Aesar, 97% purity) were charged in the vials in order to have powder mixtures consisting of MgH_2 + 5 mol.% FeF_3. The milling was carried out for 48 h with a ball-to-powder weight ratio, which exceeded 20:1. All the powder handling before and after milling was carried out in a glove box under a protecting argon atmosphere.

Small Angle Neutron Scattering (SANS) was performed at D16 instrument, ILL (Institute Laue Langevin) in Grenoble using a wavelength λ = 4.53 Å. For each series of acquisitions, around 150/200 mg of powders were loaded into an aluminium sample holder. The system was evacuated ($P \approx$ 100 Pa) to allow desorption, whereas a deuterium

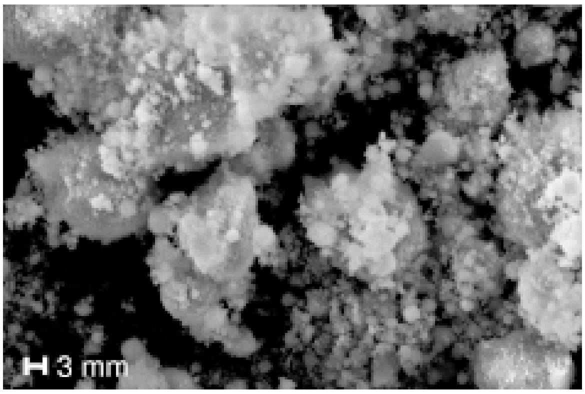

Fig. 2. SEM picture of as-milled MgH_2 powders. The powder particle aggregates show self-similarity features, which are typical of fractal structures.

pressure of about 0.8 MPa was reached for absorption. A moving detector allowed to carry out measurements at both small and wide angles. In the latter case, the [110] peak of MgD_2 and the [101] peak of Mg were monitored in order evaluate the extent of the absorption/desorption reaction. The powders were heated in situ by means of a gas blower pointing at the sample holder. The gas blower allowed to reach temperatures of up to about 625K.

3. RESULTS AND DISCUSSION

Fig. 1 shows typical SANS curves, in which the logarithm of the scattered intensity $I(q)$ is plotted as a function of $\log(q)$, q being the scattering vector. The latter is defined as $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle and λ is the neutron wavelength. It can be noticed that, for 0.02 Å^{-1} $< q <$ 0.15 Å^{-1}, $I(q)$ obeys a power law, which can be described by the equation [7,8]

$$I(q) = 10 \quad q^{-} \quad , \; a \tag{1}$$

where α and I_0 are constants. The magnitude of the exponent α, which can be evaluated by a linear fit of the $\log(I(q))$-$\log(q)$ relation, can give information on the nature of the structure producing the scattering. For instance, if $\alpha = 4$, then Porod's law is satisfied. This indicates that scattering results from randomly oriented scattering elements with a sharp interphase boundary associated with smooth surfaces [9]. It is worth mentioning that Eq. 1 is usually observed when the scattering vector q fulfils the condition $q\xi > 1$, where ξ is a length that characterizes the scattering elements.

In the room-temperature SANS curves for two different batches of ball-milled MgH_2 + 5 mol.% FeF_3 composite powders (curves a and b in Fig. 1), the linear fit yields a power-law scattering exponent of $\alpha = 2.47$ and 2.28, respectively, which is well below the value expected for Porod's law. Such a kind of positive deviation from Porod's law is usually observed when the scattering entity is a mass fractal or a surface fractal [8].

The power law scattering exponents for mass and surface fractals are found to be $\alpha = D$ and $\alpha = 6 - D$, respectively, D being the fractal dimension [7]. Since mass fractals are characterized by a fractal dimension $D \leq 3$ and for surface fractals $2 \leq D \leq 3$ [10], it follows that $\alpha \leq 3$ for mass fractals, whereas, for surface fractals, $\alpha > 3$. It is worth noticing that a surface fractal with $D = 2$ corresponds to a smooth surface and, according to $\alpha = 6 - D$, results in a power-law scattering exponent of 4. The latter is the value expected when Porod's law apply – i.e. when the scattering results from sharp smooth boundary surfaces.

According to the above discussion, the power-law scattering exponents found for the two as-milled samples can be related to mass fractals with fractal dimension $D = 2.47$ and $D = 2.28$, respectively. It is likely that such a fractal structure stems from the powder particle aggregates, which usually result after ball milling. Typical powder particle aggregates can be observed in Fig. 2, which shows an SEM picture of as-milled MgH_2 powders. In Fig. 2, self-similarity features, which are characteristic of fractal structures [7], can be observed. It should be mentioned that fractal geometries have already been observed, by SANS, in ball milled powders [11].

SANS measurements were performed upon cycling, and the changes of the power-law exponent α related to absorption and desorption could be monitored. As an example, the SANS curve after one desorption/ absorption cycle is shown in Fig. 1 (curve c). It can be noticed that the slope, where the linear behaviour is observed, is larger than that observed for the as-milled powders. In particular, it is found that $\alpha = 4.08$, clearly indicating that the structure producing the scattering have undergone some change.

Fig. 3 shows the values for α, as calculated from the SANS curves taken during three desorption and absorption cycles. After the first desorption the power-law exponent increases to about 3.5. This value can be related to surface fractals with fractal dimension $D \approx 2.5$. The reason for such a change

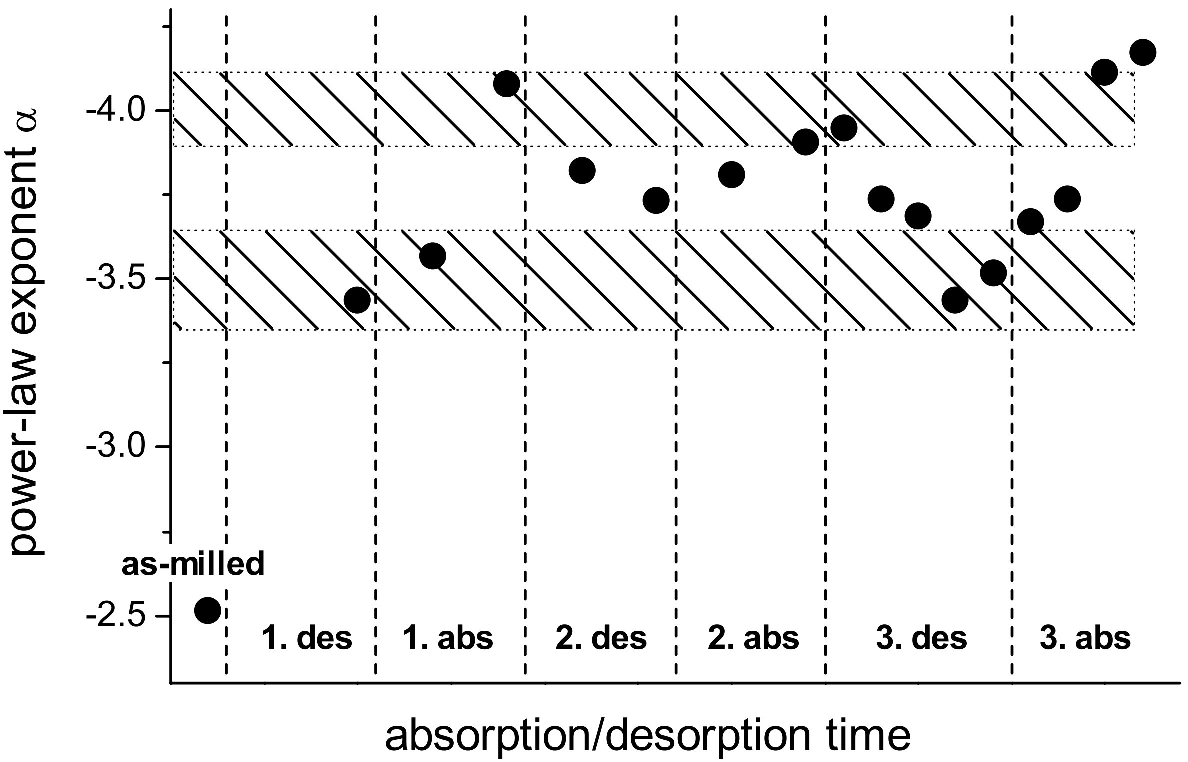

Fig. 3. Values for the power-law exponent α during cycling, as resulted from a linear fit of the SANS curves. The upper shaded area is where Porod's law is satisfied, whereas the lower one indicates the region where surface fractals with $D \approx 2.5$ are observed.

can be explained by taking into account two different processes that might occur during desorption.

First of all, because of heating of the powders to temperatures as high as 575K, changes of the powder morphology due to sintering cannot be ruled out. In particular, sintering can involve the self-similar aggregates, which characterize the powders in the as-milled state, and, in turn, affect the fractal geometry of the powder. Then, most importantly, due to the large difference in density of MgH_2 and Mg, a significant shrinking in volume should be expected, which is likely to result in a pronounced pore structure. Indeed, an exponent $\alpha > 3$ can arise from both surface scattering from rough pore walls or bulk scattering from a porous media having a sufficiently wide pore size distribution [12].

During the first absorption α increases slightly and, as mentioned above, reaches a value of about 4 when absorption is complete. Hence Porod's law is satisfied, indicating that scattering results from extended scatterers with smooth (i.e. non-fractal) boundary surfaces. The disappearance of the fractal geometry can be related again to the change in volume, which occur upon absorption. As the reaction $Mg + H_2 \rightarrow MgH_2$ proceeds and the volume expands, the pore structure, which developed during desorption, vanishes. Upon further cycling, α changes continuously between about 3.5 and 4 after desorption and absorption, respectively, suggesting the development of a pore structure when Mg forms and its disappearance when MgH_2 forms. Further investigations and analysis (e.g. scanning electron microscopy, BET analysis) are required to confirm the occurrence of surface self-similarity, as well as the presence of a pore structure in the dehydrided state. Such analysis could help to better understand the relation between fractal structures with a given fractal dimension *D* and the H-sorption behavior of ball-milled MgH_2 composite powders containing FeF_3. Furthermore, it could be interesting to see if such a relation exists when different catalysts are added to MgH_2 during ball milling (e.g. transition metals or transition-metal oxides) and if it applies to other hydrogen storage materials.

4. SUMMARY

The H-sorption behaviour of ball-milled MgH_2 containing 5 mol.% FeF_3 was studied by in-situ Small Angle Neutron Scattering. A power-law regime is observed, indicating the presence of fractal geometries in the as-milled powders (mass fractal of fractal dimension $D \approx 2.4$) and after desorption (surface fractals with D of about 2.5), whereas Porod's law is satisfied after absorption cycles.

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