

Letter

Effect of ball milling on the hydrogen absorption rate of FeTi and Mg₂Ni compounds

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1. Introduction

The intermetallic compounds FeTi and Mg₂Ni are the most useful hydrogen storage alloys [1, 2]. One of the drawbacks of these alloys is that they absorb hydrogen very slowly unless the activation treatment has been performed. The alloys are generally activated by performing a number of heating-cooling and hydrogen absorption-desorption cycles. Although the nature of the activation process is not as yet fully understood [3-5], the proposed mechanisms are grouped roughly into two categories. In the first, the activation treatment of FeTi gives rise to the precipitation of Fe-rich clusters close to its surface and these clusters catalyse the decomposition of molecular hydrogen. In the second category, the activation treatment leads to structural and morphological changes of the powder surface, *i.e.* to the formation of the fresh surface free of an oxide layer. However, it is well known that fresh surfaces and cracks are created by the ball milling of metals and intermetallic compounds [6]. Consequently, if the samples milled in an inert gas atmosphere are hydrogenated without the exposure to the air, hydrogen is expected to be readily absorbed. In this work, FeTi and Mg₂Ni compounds ball milled in different atmospheres are hydrogenated without exposure to the air to make clear the effects of milling atmosphere on the initial hydrogen absorption rate of these compounds.

2. Experimental details

The equiatomic FeTi compound was prepared by arc melting in an argon atmosphere and pulverized into

powder (-115 mesh). Mg₂Ni was prepared by argon induction melting and pulverized into powder (-50 mesh). These powder samples were put into a SUS 316 stainless steel container together with SUS 316 stainless steel balls (3/8 inch diameter). The ball-to-powder weight ratio was 13/1 for FeTi and 20/1 for Mg₂Ni. A vial and a lid were sealed with a viton O-ring. Before milling, the container was evacuated for 10 ks by a diffusion pump (2×10^{-5} torr). Ball milling was performed using a high energy planetary ball mill (Fritsch P5) for different periods in a vacuum and in an argon and hydrogen atmosphere. Immediately after ball milling and degassing (H₂ and Ar atmosphere), the samples were hydrogenated in the container with the pressure sensor at 2 MPa H₂. The amount of absorbed hydrogen was evaluated from the pressure drop in the constant inner volume of the container as a function of time.

3. Results and discussion

Figure 1 shows the hydrogen absorption curves of the FeTi powders at 283 K and 2 MPa H₂ after ball milling for 0, 1.8, 10.8 and 86.4 ks in an argon atmosphere. The longitudinal axis represents the hydrogen content, H/M, expressed by the number of hydrogen atoms per metal atoms. No hydrogen absorption is observed in the original sample (0 ks milling). On the contrary, hydrogen is readily absorbed in the samples

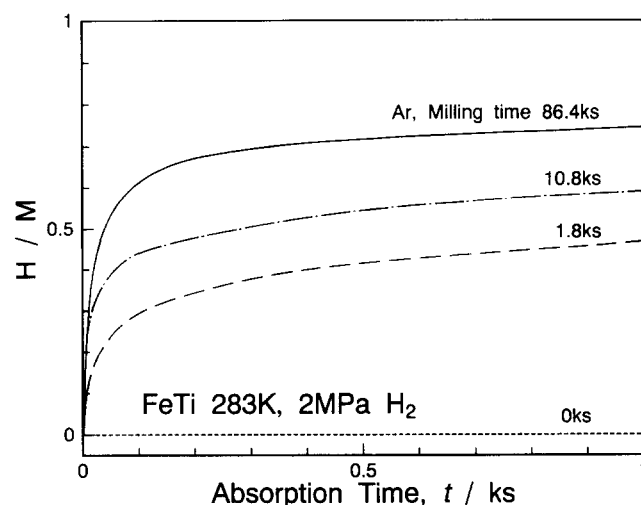


Fig. 1. The hydrogen absorption curves of the freshly prepared FeTi samples at 283 K and 2 MPa H₂ after ball milling for 0, 1.8, 10.8 and 86.4 ks in an argon atmosphere.

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ball milled for 1.8 ks or more in an argon atmosphere. As the milling time increases, hydrogen is absorbed more rapidly, particularly at the initial stage between 0 and 0.1 ks. If the ball milled sample is exposed to the air even for a short time, 0.2 ks, it does not absorb hydrogen again as shown in Fig. 2. This result indicates that no exposure of the sample to the air is very effective for the improvement of the initial hydrogen absorption rate.

Figure 3 shows scanning electron micrographs (SEM) of the original sample and the ones ball milled for 1.8 and 86.4 ks in an argon atmosphere. These powder samples were exposed to the air for 0.2 ks to observe their morphology and the surfaces are considered to be covered by thin oxide layers. These micrographs have been taken to show the changes in their morphology and their particle size. The original sample shows the flat and cleavage fracture surface morphology and the average particle size is about $50 \mu\text{m}$. On the contrary, the shape of the sample ball milled for 86.4 ks is spherical and the average particle size is reduced to about $5 \mu\text{m}$. Thus the fracture and fragmentation of FeTi powders during ball milling increase drastically the surface area.

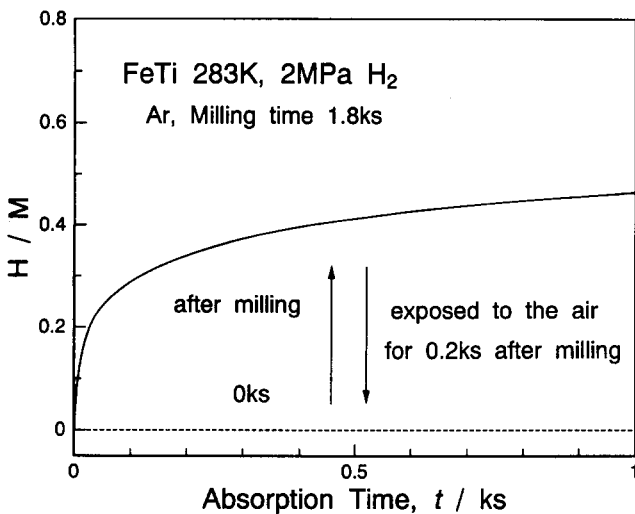


Fig. 2. The hydrogen absorption curves of the freshly prepared FeTi powder after ball milling for 1.8 ks in an argon atmosphere and subsequently exposed to the air for 0.2 ks.

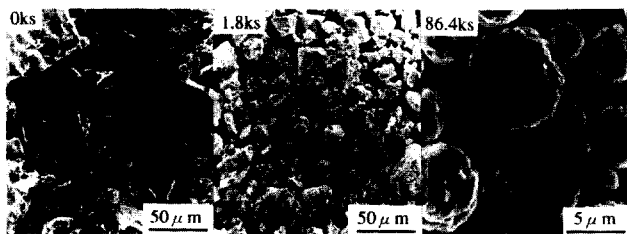


Fig. 3. SEM images of the original sample and the ones ball milled for 1.8 and 86.4 ks in an argon atmosphere.

Figure 4 shows the effect of the ball milling atmosphere on the initial hydrogen absorption rate of FeTi. In the case of the samples ball milled in Ar and H_2 , gases are desorbed using the vacuum pump. Hydrogen is absorbed most quickly into the sample ball milled in a vacuum. This result is reasonable, because the surfaces created by ball milling in a vacuum are generally known to be most clean and reactive.

Figure 5 shows the effect of ball milling of Mg_2Ni on their initial hydrogen absorption rate. The original sample (0 ks milling) does not absorb hydrogen, while the samples ball milled for 0.06 ks or more in an argon atmosphere can absorb hydrogen. As the milling time increases, hydrogen is absorbed more rapidly.

The hydrogen absorption alloy powders are industrially prepared by either crushing in the air or ball

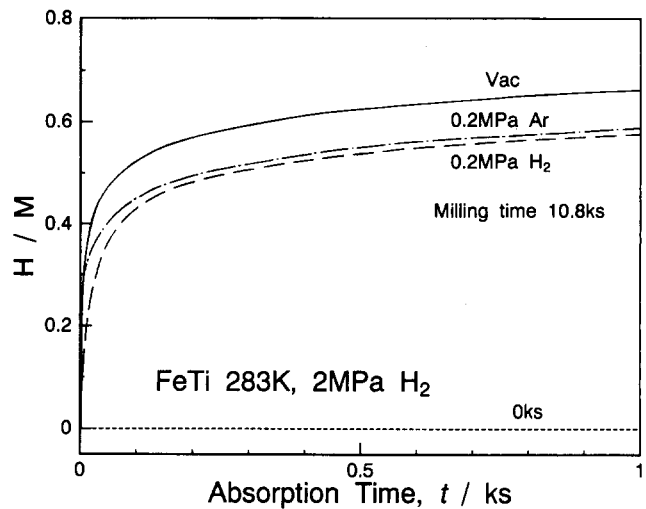


Fig. 4. The effect of the atmosphere during ball milling on the initial hydrogen absorption rate.

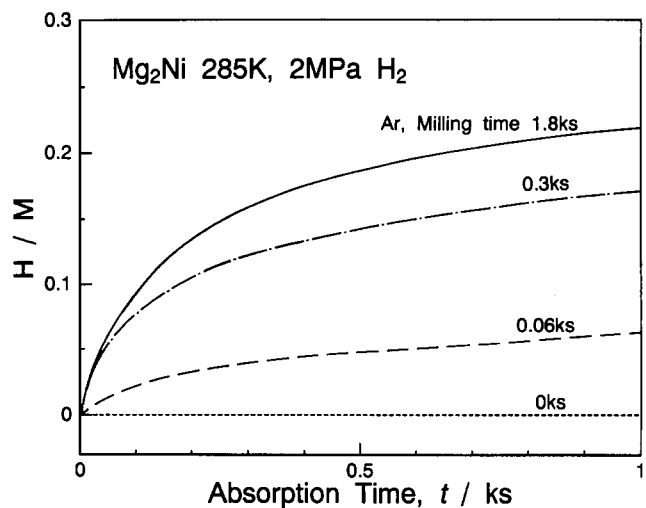


Fig. 5. The hydrogen absorption curves of the Mg_2Ni powder at 283 K in 2 MPa H_2 after ball milling for 0, 0.06, 0.3 and 1.8 ks in an argon atmosphere.

milling in an inert gas atmosphere. Even if the alloys are ball milled in an inert gas atmosphere, they are usually exposed to the air when they are transferred from the milling container to the hydrogen absorption reactor and obviously such samples are covered by a thin oxide layer. The present work clearly demonstrates that ball milling in an inert gas atmosphere and in a vacuum, which gives rise to the creation of fresh surfaces and cracks, is effective for the improvement for the initial hydrogen absorption rate of FeTi and Mg₂Ni when they are not exposed to the air. This technique can be applied to the other hydrogen absorption alloys which can hardly absorb hydrogen at first. The present experimental data strongly support the model that the activation mechanism of FeTi and Mg₂Ni is closely related to the creation of fresh surfaces and cracks.

In conclusion, ball milling of FeTi and Mg₂Ni compounds in an argon and hydrogen atmosphere and in a vacuum is very effective for the improvement of their initial hydrogen absorption rate.

References

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