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研究課題名（和文）Mechanism of Activation of TiFe for Hydrogen Storage by High-Pressure Torsion

研究課題名（英文）Mechanism of Activation of TiFe for Hydrogen Storage by High-Pressure Torsion

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研究成果の概要（和文）：本研究では、結晶粒界の重要性を調査するため、次のような４つのTiFe合金を準備して調べた。焼鈍したTiFe合金は水素吸収を示さなかった。溝ロールで圧延した場合は、サブミクロンサイズの亜結晶粒が形成し、部分的に水素吸収を示した。HPT加工したり ボールミルした場合は、ナノサイズの結晶粒が形成し、水素吸収は完全に生じた。したがって、ナノサイズの結晶粒が生じると、TiFeは容易に活性化されることになった。
本研究では、Mg2Niの水素吸蔵特性についても調べた結果、TiFeと同様な結果が得られ、高密度の結晶粒界は水素貯蔵合金の活性化に有効であることが知られた。

研究成果の概要（英文）：TiFe intermetallic, a candidate for hydrogen storage, does not absorb hydrogen easily because of difficult activation, while TiFe processed by HPT absorb hydrogen. We showed that the activation is due to (i) enhanced diffusion, (ii) surface segregation of Fe-rich islands and (iii) formation of grain boundaries.
To investigate the importance of grain boundaries, TiFe was processed by 4 routes. The annealed sample, with micrometer grain sizes, didn't absorb hydrogen. The groove-rolled sample, with submicrometer subgrain sizes, was partially activated. The HPT-processed and ball-milled samples, with nanograins, were fully activated. Therefore, the activation becomes easier when nanograins form.
Mg2Ni intermetallic was also processed by HPT and its hydrogenation was examined. While Mg2Ni after annealing absorbed hydrogen partially, the HPT-processed sample fully absorbed hydrogen at 423 K. It was concluded that the large fractions of grain boundaries are responsible for activation.

研究分野：　Hydrogen Storage Materials

キーワード：　Hydrogen Storage　Energy Storage　Severe Deformation　High-Pressure Torsion　Activation　Deactivation　Metal Hydrides　Ultrafine Grains

１．研究開始当初の背景

TiFe intermetallic compound is a potential candidate for the solid-state stationary hydrogen storage systems, but it does not absorb hydrogen without an activation process because of surface oxidation. However, TiFe severely deformed by high-pressure torsion (HPT) absorbs and desorbs hydrogen at room temperature without activation process. The mechanism underlying this activation by HPT processing was not reported in the earlier publications.

２．研究の目的

The purpose of this research was to understand the activation mechanism by HPT and investigate the effect of processing parameters on this activation.

３．研究の方法

TiFe is severely deformed using HPT under different conditions of shear strain to investigate the activation mechanism for hydrogen storage. The surface condition and oxidation are examined by scanning electron microscopy, X-ray photoelectron spectroscopy and Auger electron spectroscopy, and the internal microstructure of the samples is examined using different techniques of electron microscopy.

In order to understand the activation mechanism, plastic strain was also introduced in TiFe samples using other processing techniques such as groove rolling and ball milling at room temperature. Moreover, another intermetallic compounds as Mg_2Ni, which partially suffers from difficult activation, was processed by HPT method and its activation was investigated at a temperature of 423 K.

４．研究成果

We showed that TiFe processed by HPT method for various levels of strain (i.e., various numbers of turns) absorb and desorb hydrogen at room temperature without any extra activation process. It was shown that the activation of TiFe sample is due to (i) enhanced diffusion of hydrogen, (ii) segregation of catalytically active Fe-rich phase and (iii) formation of large fraction of grain boundaries as pathways to transport hydrogen through the oxide layer. The schematic illustration of activation mechanism is shown in Fig. 1.

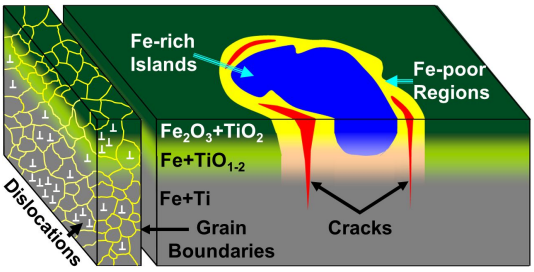

Fig. 1. Schematic illustration of activation mechanism of TiFe by HPT.

In order to investigate the importance of grain boundaries, TiFe was processed by four different routes and the activation was investigated. The microstructures of samples processed by these routes are shown in Fig. 2.

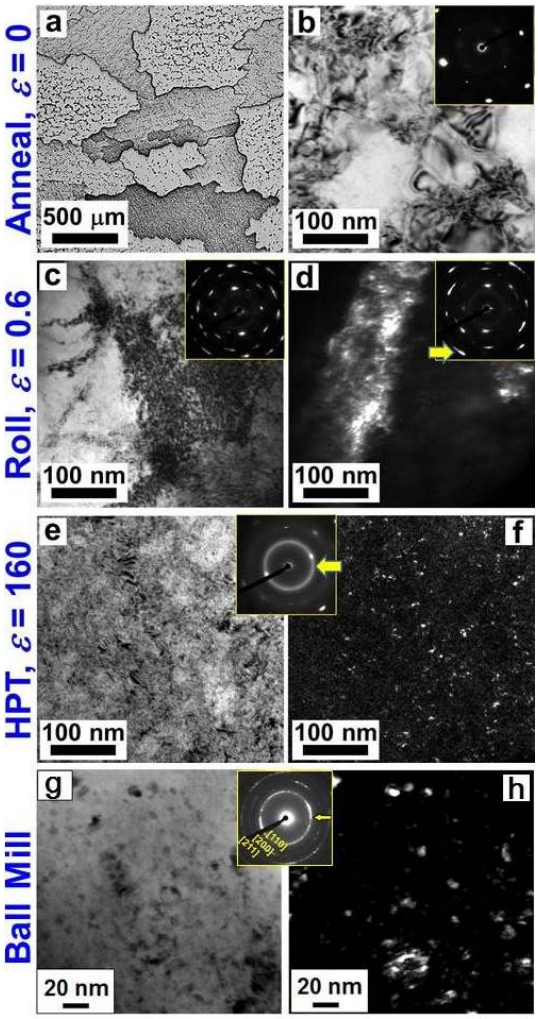

Fig. 1. Microstructure of TiFe samples after (a,b) annealing, (c,d) groove rolling, (e,f) HPT, and (g,h) ball milling.

As shown in Fig. 3, the annealed sample, with micrometer grain sizes, did not absorb hydrogen. The groove-rolled sample, with

submicrometer subgrain sizes, was partially activated. The HPT-processed sample, with grain sizes in the range of nanometer to submicrometer, was fully activated under 2 MPa. The ball-milled sample, with nanometer grain sizes, was fully activated under 1 MPa. Therefore, the activation becomes easier when the grain size is smaller.

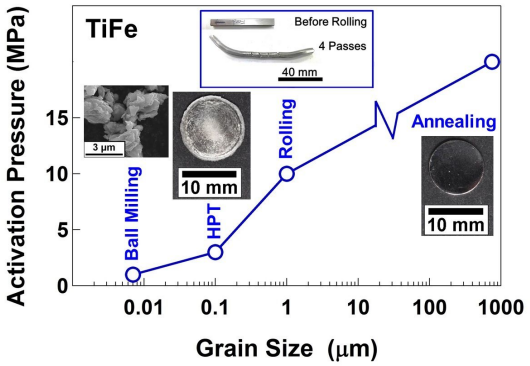

Figure 1. Decreasing activation pressure of TiFe by decreasing grain size.

In order to investigate the effect of grain boundaries on activation, another intermetallic, Mg_2Ni, was processed by HPT. While Mg_2Ni after annealing absorbed hydrogen partially, in the first hydrogenation cycle, as shown in Fig. 4, the HPT-processed sample fully absorbed hydrogen at 423 K from the first hydrogenation cycle. The current part of study also confirms that the large fractions of grain boundaries are responsible not only for activation of TiFe but also for activation of Mg_2Ni.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　４　件）

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〔図書〕（計　0　件）

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〔その他〕
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