EFFECT OF REACTIVE MILLING ON THE MAGNETIC BEHAVIOR OF Mg$_2$FeH$_6$ BASED METAL HYDRIDES

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ABSTRACT

In this work, the magnetic behavior of ternary hydride compound Mg$_2$FeH$_6$ have been studied by means SQUID measurement at fields up to 4.5 T with the temperature between 1.7 and 293 K. The samples were milled under a hydrogen pressure of 7 bar in a planetary ball mill (Fritsch P6). The pressure was constantly monitored with a hydrogen pressure sensor (GTM sensor Fritsch) and the vial was refilled when the hydrogen pressure decreased to 1 bar. Synthesis of Mg$_2$FeH$_6$ by reactive milling MgH$_2$ with Fe under H$_2$ atmospheres were investigated in order to optimise the conditions of forming Mg$_2$FeH$_6$. The samples have also been characterized by X-ray diffraction (XRD) in order to know the phase composition. The result show that the magnetization decreases with the increasing milling time.

Keywords: hydrogen, reactive milling, magnetic behavior, metal hydrides

INTRODUCTION

Hydrogen plays a crucial role in the properties of various materials. The use of hydrogen in assisting in the production of fine powders has been reported widely$^1$. Metal hydrides for blending have several advantages over the use of pure metals$^2$:

a. Expansion of the lattice during hydriding assists the breaking up of the bulk alloy into particles suitable for milling.
b. Hydrides are usually brittle and readily milled.
c. The rare earth dihydride powders are more stable than the corresponding metal powders, reducing the incorporation of oxygen during processing.
d. Once the hydrogen is desorbed, the powder becomes very reactive, which aids in-situ alloying.
e. It is possible that the presence of hydrogen enhances solid-state diffusion.

The ternary hydride compound, Mg$_2$FeH$_6$ shows a high hydrogen-storage capacity of 5.5 wt%, and it is desirable for hydrogen storage. However Mg$_2$FeH$_6$ is more difficult to synthesize than the conventional transition metal hydride. Firstly, Didisheim et al.$^3$ showed that Mg$_2$FeH$_6$ could be synthesized by sintering Mg and Fe powders at around 500 °C under 60–120 bar of H$_2$ pressure. Huot et al.$^4$ firstly reported a high yield of 65 wt% Mg$_2$FeH$_6$ by milling (2Mg + Fe) under H$_2$ atmosphere for 20 h, and subsequent sintering at 623 K under 50...
bar Hydrogen. Gennari et al.\(^5\) reported that reactive mechanically alloying the mixture of \((2\text{Mg} + \text{Fe})\) in 5 bar of \(\text{H}_2\) atmosphere led to the formation of \(\text{Mg}_2\text{FeH}_6\). However, the yield after 60 h of milling was only 30 wt\%. Raman et al.\(^6\) achieved 63 wt\% \(\text{Mg}_2\text{FeH}_6\) under a \(\text{H}_2\) pressure of ~10 bar after only 20 h of high-energy milling. As \(\text{Mg}_2\text{FeH}_6\) is one of the candidate materials for hydrogen storage, it is also interesting to know the magnetization behavior in the sense the iron substitutional in the material.

It is well known that the absorption of hydrogen gas in intermetallic compounds often leads to spectacular changes in their magnetic properties. In intermetallics where the magnetism is due to 3d elements these changes include the paramagnetic-to-ferromagnetic transition observed in several manganese and iron compounds and the ferromagnetic-to-paramagnetic transition found in several cobalt and nickel compounds\(^7\). Some investigations have been made in past few years, in case of the effect of hydrogen on the magnetic behavior of alloys\(^8,9,10\).

In this work, the synthesis of \(\text{Mg}_2\text{FeH}_6\) by reactive milling \(\text{MgH}_2\) with Fe under \(\text{H}_2\) atmospheres were investigated in order to optimise the conditions of forming \(\text{Mg}_2\text{FeH}_6\). The phase composition was investigated by X-ray diffraction. Then, the magnetic behavior measured by using Superconducting Quantum Interference Device (SQUID) at fields up to 4.5 tesla.

**RESULTS AND DISCUSSION**

The XRD evolution can be seen in Figure 1 which has already been done elsewhere\(^11\).

Figure 1 showed the X-ray diffraction patterns using Co-K\(_\alpha\) radiation of \((2\text{MgH}_2 + \text{Fe})\) mixture milled in a planetary ball mill for various durations at room temperature during reactive milling. It shows the evolution of the XRD diffraction pattern for \(2\text{MgH}_2 + \text{Fe}\) as a function of milling time. It can be seen that during milling the \(\text{MgH}_2\) and Fe diffraction peaks broaden but no changes in the 2θ position before 40 h milling times. After 4 h milling the peaks are broader, and also during 4 h...
milling a small peaks of metastable $\gamma$-MgH$_2$ peaks appears.

After prolonged milling times the MgH$_2$ peaks disappear and the reaction is complete to produce Mg$_2$FeH$_6$ phase. Also there was a small peak of MgO after 80 h milling. The presence of MgO is possibly due to oxygen during measurement in the air, during milling work (pick-up the sample). The X-ray diffraction pattern after 80 h milling times are extremely broader. This indicate that the crystallite size getting tens nanometer.

The Mg$_2$FeH$_6$ peaks appears after 20 h, but the reaction is still incomplete yet.

The variation of magnetization with milling time is shown in Fig. 2. The sample with 20 h, 42 h, and 80 h was used in SQUID experiment. From the experimental results of the investigation into the hydrogenation effect on magnetization properties, it can be seen that the magnetization decreases during milling. It is also well known that with increasing milling time, will also increase the hydrogen content in the compound.

Fig. 1: X-ray diffraction patterns using Co-K$\alpha$ radiation of (2MgH$_2$ + Fe) as a function of the milling time

Fig. 2. Magnetic measurement of Mg$_2$FeH$_6$ using SQUID up to 4.5 tesla at 293 K with various milling time
Compare to our result for magnetic behavior of Mg-Ni-Pd\textsuperscript{12}, it was also found that the magnetic properties of magnesium hydrides significantly depend on the milling time. After longer milling time, the magnetization decreased. This results in the decrease of the long-range exchange interaction. The magnetism in this material being itinerant due to the presence of Ni and Pd, the magnetic moments depends on the exchange interactions that depend on the interatomic distances. Therefore, in the presence case, the magnetization is expected to decreased with milling time.

In simplified view the effect of hydrogen absorption upon the magnetic properties in transition metals and their intermetallics is twofold\textsuperscript{13}. First, the presence of hydrogen perturbs the metal-metal bonds by creation of metal-hydrogen interactions. Second, hydrogen absorption commonly results in a volume expansion (i.e., negative pressure), which influences not only the strength of the magnetic exchange interaction between localized/delocalized electrons but increases also the extent of localization of their associated magnetic moments. In other words, a larger volume implies narrower bands which, on the one hand, gives rise to more localized moments and, on the other hand, may reduce the hybridisation of different electronic states present in the host compound.

This phenomenon is interesting in the sense that the magnetization decreases with milling time. Some researchers explained this due to the decreasing of particle size during milling. The reduction in particle size causes disordering at the surfaces that may also cause a reduction/decreasing in magnetization. Boudart \textit{et al.} \textsuperscript{14} in 1977 have studied the effect of chemisorption of hydrogen on magnetic anisotropy using Mössbauer spectrometer. The focus was on the surface, catalytic, and magnetic properties of small iron particles. It was shown that the superparamagnetic behavior of very small particles of metallic iron (\textit{ca} 1.5 nm), with about half of their atoms at the surface, is changed reversibly by adsorption and desorption of hydrogen below the superparamagnetic transition temperature. The change after adsorption implies a lowering of the anisotropy energy barrier for the magnetic relaxation of iron and ascribed to a change in crystalline shape. No such changes are observed for larger particles of iron (\textit{ca} 8 nm) with about 10\% of their atoms at the surface.

All the Boudart’s data indicate that chemisorbed H\textsubscript{2} decreases the magnetic anisotropy barrier of small iron particles but has no observable effect on the superparamagnetic behavior of larger ones. More recently, Chelvane \textit{et al.} \textsuperscript{15} reported similar result in TbFe\textsubscript{2} and TbFe\textsubscript{2}B. The magnetization was found to decrease rapidly up to 30 h of initial milling time. It was also found to be constant with further milling time as has been attributed to the localization of Fe moments with decrease in particle size.

**CONCLUSION**

In this paper, the effect of reactive milling on the magnetization of Mg\textsubscript{2}FeH\textsubscript{6} metal hydrides alloy has been investigated. The results show that after longer milling time, the magnetization decreased. Therefore, it can be concluded that the longer milling time, the lower magnetization. The magnetization decreases with the increase of milling time may be attributed through the reduction in particle size of the milling samples.

**REFERENCES**


