Synthesis of the nanocrystalline MgS and its interaction with hydrogen

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Abstract

Nanocrystalline MgS was directly synthesized from MgH_2 and S powders by high energy ball milling in Ar atmosphere. The X-ray diffraction peaks revealed the formation of MgS phase with NaCl-type structure, and showed no evidence of any secondary phase. The average grain size estimated by the diffraction line profile analysis was about 11 nm, and was confirmed by TEM studies. SEM investigations show that the average particle size of the powder was below 10 μm. At room temperature, no significant reaction with hydrogen was observed. At liquid nitrogen temperature (77 K), the storage capacity was only 0.5 wt.% at 50 bar H_2 pressure, which may be limited by the specific surface area.

These results indicate that the interaction between H_2 molecules and the nanocrystalline MgS is weak, of the order typical for physisorption.
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1. Introduction

The dihydrogen metal complex was discovered firstly by Kubas in 1988 [1]. In the dihydrogen complex, the hydrogen appeared to be bound to a metal center as a molecule rather than dissociated hydrogen atoms, and the bonding of the hydrogen molecule to the metal was related to the electron donation from the filled H_2 orbital to empty the metallic d orbital. This kind of bonding is very scarce. Normally, the hydrogen molecule is adsorbed only in the physisorbed state, owing to the weak van der Waals interaction. Chemical bonding requires a dissociation of the hydrogen molecule into two hydrogen atoms. After the discovery of Kubas [1], a series of complexes with different ligand or metal clusters have been identified [2–4] and moreover, the molecular chemisorption of hydrogen on nickel surface was observed [5]. Motivated by these findings, the possibility of complex compounds of $BeSH_2$, $BeOH_2$, and $MgSH_2$ was theoretically calculated [6–8]. For the formation of these compounds including non-transition metals, it is thought that the metal centers do not need to have d orbitals to form a bonding with H_2 molecules without dissociation. This type of compounds can actually trap the hydrogen molecules, and this phenomenon may be applicable for hydrogen storage. In a view point of actual chemical reaction, it is necessary to consider the potential energy surfaces of the reaction for each compound. In case of $BeSH_2$ compound, the ab initio calculation of the $BeS + H_2 = SBeH_2 = HBeSH = Be + H_2S$ reaction revealed that there was a sufficient local energy minimum for the easy adsorption of hydrogen. According to the calculation [6], if the hydrogen were charged to the BeS molecule, BeS could easily absorb hydrogen molecule as $BeSH_2$ dihydrogen complex and there would not be any energy barrier. After $BeSH_2$ formation, the reaction might proceed to isomerizes into HBeSH compound with a low energy barrier of 29.26 kJ/mol. Ultimately, the HBeSH molecule possessed a binding energy of 233.2 kJ/mol, and was thermodynamically stable enough to be used as a hydrogen storage medium. However, the stumbling block for realizing this theoretical prediction is on the toxicity of elemental Be. The handling or practical use of Be as a hydrogen storage medium seems not to be reasonable. On the other hand, among the compounds suggested above, the MgS compound is expected to possess potential surfaces similar to BeS concerning the reaction with hydrogen. Therefore, MgS is selected for this study. We try to synthesize nanocrystalline MgS compound by ball milling of MgH_2 and S powders, and investigate the hydriding property.

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2. Experimental

The nanocrystalline MgS powders were synthesized by mechanical milling. The MgH_2 compound and the elemental S powders were mixed to give the desired composition. These starting materials and 10 mm steel balls were put into a sealed bowl in Ar atmosphere with a pressure of 1 bar. The ball milling was performed with a ball to powder ratio of 120/1, for a maximum of 300 min at a milling speed of 400 rpm, untilizing a planetary ball mill (Fritsch P-6).

The milled powders were collected in Ar atmosphere, and characterized by X-ray diffraction with Cu Kα radiation and a secondary monochromerter. Scanning electron microscopy and TEM investigations have been performed.

The grain size of the ball-milled powders was estimated by X-ray diffraction profile analyses. The observed profile was fitted to the Pseudo–Voigt function to get the integral breadth. Since the measured line profile directly from the diffractometer, h is the convolution of the standard profile or instrumental broadening, g with the structurally broadened profile, f, in order to separate the pure structural broadening, f, we need to know the instrumental broadened profile, g [9,10]. This relation is expressed as follows:

$$h = gf$$

We used the diffraction profile of the annealed MgS powders at 500 °C, i.e. after crystal growth to large grains, as an instrumental broadening g, and get integral breadth, $β$ values for structural broadened profile, f. Then the grain size was calculated by the following equation [9,10]:

$$D = \frac{1.5405\,\text{Å}}{\beta\cos\theta} \times 57.3$$

The hydrogen storage capacities were measured at temperatures of 77 and 300 K using a conventional Sieverts' type apparatus, which was designed for the measurement of small sample mass. For each measurement, about 100 mg of powder was charged into the stainless steel reactor. Prior to the measurement the sample was degassed at 200 °C, 10^{-6} mbar.

3. Results

3.1. Structural properties of ball-milled powder

The X-ray powder diffraction patterns of the ball-milled powders are shown in Fig. 1 for different milling time. From initial state to 20 min in Fig. 1(b), MgH_2 and elemental S peaks are clear by visible. After a milling duration of 40 min, the MgS compound had been formed, and with longer milling time the peaks of MgS were broadened. For long milling time, near about 43° a maximum arises which may be caused by metallic impurities due to the wear of the balls and bowl. The synthesized MgS had NaCl sturucture, and the lattice parameter was estimated to 5.17 Å.
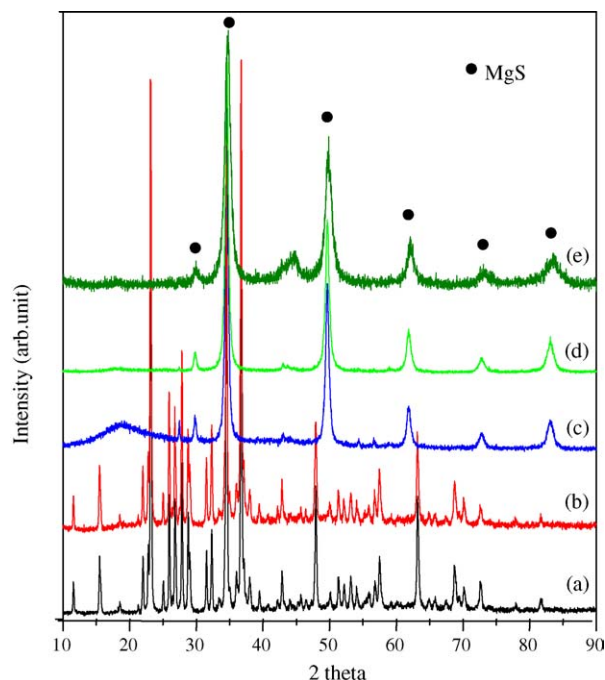

Fig. 1. XRD spectra of the ball-milled powder: (a) initial mixture; (b) milled for 20 min; (c) milled for 40 min; (d) milled for 60 min; (e) milled for 300 min.

Fig. 2 shows the diffraction pattern for the powders after milling for 300 min. The grain sizes obtained from the 200, 220, and 222 single lines are 11.3, 8.41, and 16.7 nm, respectively (Table 1). The grain size was confirmed by TEM. These results confirm that a nanocrystalline MgS compound was directly synthesized by ball-milling of MgH_2 and S powders.

Fig. 3 shows the SEM micrographs of the powders of the initial state, and the nanocrystalline MgS. After ball-milling, each particle is highly refined, and the size is below 10 μm.
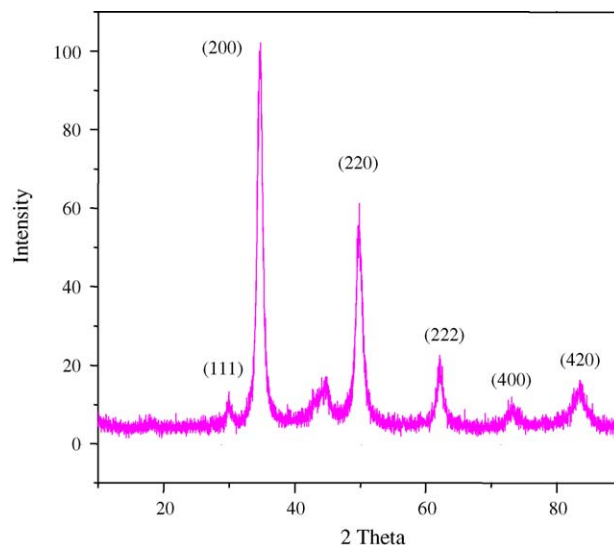

Fig. 2. XRD spectra of the nanocrystalline MgS powder.

Table 1
Calculated grain size from the single line analyses

2θ	hkl	Voigt broad-beta	Grain size (nm)
34.72	200	0.8166	11.3
49.85	220	1.1573	8.41
62.16	222	0.6159	16.7

3.2. Hydrogen storage properties

The hydrogen storage capacity of nanocrystalline MgS powders for pressures up to 50 bar is shown in Fig. 4 for two different temperatures of 77 and 300 K. At 300 K, the absorbed capacity was less than 0.1 wt.%, and at 77 K, was 0.5 wt.%. This indicates that the interaction energy between hydrogen and nanocrystalline MgS is very low and may be only in the order typical for physisorption. The theoretical calculations of the formation of dihydrogen–metal complex are typically performed on a single MgS cluster [6–8]. Therefore, in an experiment with powder particles an adsorption may be expected only at the surface, and the surface area accessible for hydrogen may play a crucial role.

The specific surface area of our powders was determined to about 20 m^2/g using nitrogen adsorption and evaluated
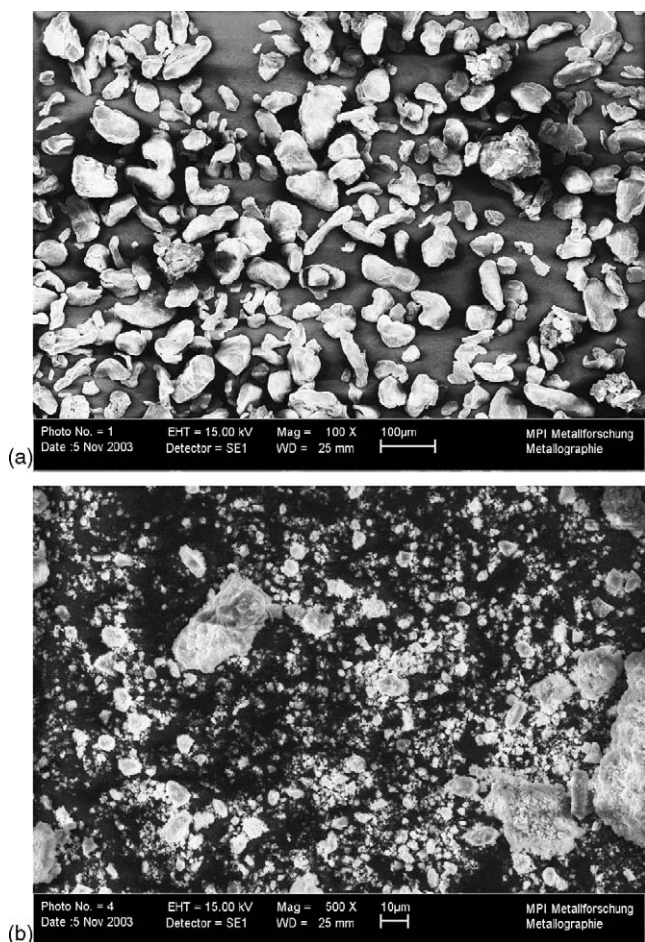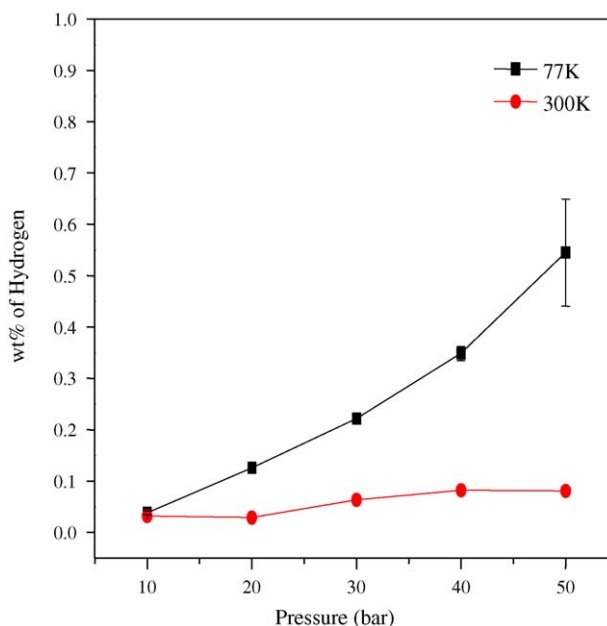

Fig. 4. Hydrogen absorption properties of nanocrystalline MgS.

according to the BET method. Owing to the fracture and rewelding process during ball milling, it was not possible to prepare powder with a higher specific surface area.

4. Conclusion

The possibility for the reaction of MgS compound with hydrogen, which has been predicted in theoretical calculation [6], has been surveyed. The single phase nanocrystalline MgS compound was directly prepared by ball milling of MgH$_2$ and elemental S powder. The nanocrystalline MgS powder with a specific surface area of about 20 m^2/g showed only a small hydrogen absorption capacity of 0.1 and 0.5 wt.% at 300 and 77 K, respectively. This indicates that the interaction energy is low. For a further comparison with the theoretical predictions, which are based on MgS clusters, specimens with a higher specific surface area are needed.

Acknowledgement

Fig. 3. SEM images for (a) initial mixture of MgH$_2$ and S (b) after ball-milling for 300 min.

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