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Hydrogen sorption enhancement in cold rolled $LaNi_5$

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ABSTRACT

In this paper, we report the effects of cold rolling on hydrogen sorption properties of $LaNi_5$. We found that cold rolling $LaNi_5$ greatly reduces particle sizes as well as crystallite sizes. After cold rolling, the activation kinetic is highly enhanced with shorter time to reach full hydrogen capacity. Cold rolling five times offers the best compromise between high capacity and fast kinetic. For completeness, we compared cold rolling with high energy ball milling for 15 and 60 min under argon atmosphere. Results showed that 15 min of ball milling had a positive effect on the time of the first absorption, but a loss in capacity was also observed. Further milling to 60 min resulted in an important degradation of hydrogen sorption properties. We also found that sample's morphology could drastically change the first absorption kinetic. In conclusion, cold rolling is a good and simple method to enhance hydrogen sorption properties of $LaNi_5$.

1. Introduction

Ball milling has been extensively used to synthesize metal hydrides, get nanocrystalline and amorphous structures and also obtain hydrogen sorption enhancement [1–5]. Recently, the so-called severe plastic deformation (SPD) techniques such as high pressure torsion (HPT), forging, extrusion, equal angular channel pressing (ECAP) and cold rolling (CR) have been investigated for replacement of milling technique for metal hydrides [6–8]. Among these, cold rolling is particularly attractive because it is well known by the industry, easily scalable and uses less energy compared to most of the other SPD techniques and ball milling. Cold rolling is an energy efficient way to induce deformations in materials. This method could be used for the synthesis of metal hydrides, as reported for Mg–Ni systems [9,10]. Cold rolling has already been used on magnesium and Ti-based BCC alloys and was shown to improve hydrogen sorption properties [11–15]. This improvement is probably due to the nanocrystalline structure and number of defects [16]. However, Couillaud et al. [17] have showed that long time ball milling and repetitive cold rolling had a negative effect on hydrogen absorption of $TiV_{1.6}Mn_{0.4}$. Therefore, usability of particular techniques depends on the chemical and physical properties of the material considered. In this paper, we report the effect of cold rolling on another class of hydride, the so-called AB_5 alloy. The best representative of this class is certainly the $LaNi_5$ alloy which has been studied for decades mainly because of its electrochemical and hydrogen storage properties [18–21].

The hydrogen storage capacity of $LaNi_5H_6$ is around 1.4 wt.%. To get such a capacity, the activation time (first hydrogenation) is quite long and many cycles are required [22,23]. We have good reasons to believe that cold rolling will accelerate hydrogenation of $LaNi_5$ by reducing particle and crystallite sizes as well as creating defects in the structure. To test this hypothesis, we investigated the effect of cold rolling $LaNi_5$ on its hydrogen sorption properties and compared them with high energy ball milling. Another part of this study consisted in taking different specimen's shapes from $LaNi_5$ cold rolled 12 times and comparing their hydrogen sorption properties.

2. Experimental details

In this study, commercial $LaNi_5$ powder provided by Angstrom Power was used. Two cold-rolling apparatuses modified for vertical rolling were used at room temperature; one under argon atmosphere and the other one in air. Rolling was performed by placing the powder between two stainless steel plates in order to prevent contamination from the rolls. After the first roll, the powder was consolidated in plates. The plates and residual powder were collected and rolled again to the final numbers of rolling. Final plates' thickness was about 1 mm. Ball milled samples were made under argon atmosphere using a SPEX high-energy 8000 M mill with hardened steel crucible and balls. The ball-to-powder weight ratio was 10 and milling was performed for 15 and 60 min. Samples from cold rolling and ball milling under argon were kept under argon atmosphere during handling and storage. No subsequent heat treatment was performed on the alloys.

The hydrogen absorption and desorption kinetic curves were measured with a homemade Sieverts-type apparatus. All measurements were performed at 323 K with a hydrogen pressure of 1500 kPa for absorption and 5 kPa for desorption. Desorption at 100 kPa is more suitable for practical applications but for testing the effectiveness of cold rolling on sorption properties, we found that working at 5 kPa permitted faster kinetics and easier comparison. Crystal structure was analyzed from X-ray powder diffraction patterns registered on a Bruker D8 Focus apparatus with Cu Kα radiation. Crystallite size, lattice parameters and microstrain were evaluated with the Rietveld refinement method using the Topas software via the

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fundamental parameters approach [24,25]. Electron microscopy was made with a Jeol JSM-5500 SEM. To improve conductivity, a gold deposit of 37 nm was sputtered on the samples using a POLARON SC 7620 sputter coater. Atomic absorption has been done on the ball milled samples to verify the possibility of iron contamination from the balls and the crucible. The apparatus used was an atomic absorption spectrometer Varian SpectrAA with a wavelength of 372 nm.

3. Results and discussion

3.1. Morphology

Before starting, it is important to note that cold rolling and ball milling have been performed under argon atmosphere at room temperature in Sections 3.1–3.3. Morphology of as-received, cold rolled and ball milled $LaNi_5$ is shown in Fig. 1. The as-received $LaNi_5$ consists of particles ranging from 20 to 200 μm. After cold rolling, the alloy shows consolidation of the powder. Cold rolling the sample for 5 times agglomerates the powder into plates and particle size is now ranging from 1 to 20 μm. In the case of ball milling, it produces an important reduction of particle size with a different morphology. After milling, individual particles with sizes ranging from 1 to 10 μm are now lumped into larger agglomerates. After 15 min of ball milling, the agglomerates sizes are about 50–150 μm and after 60 min, they are reduced to a range from 5 to 50 μm.

3.2. Hydrogen sorption properties

Fig. 2(a) shows the first hydrogenation (activation) of all samples at 323 K under 1500 kPa of hydrogen. The as-received sample is very hard to activate under these conditions. We see that cold rolling drastically reduces the activation time. A short ball milling of 15 min also greatly reduces the activation time mainly by the absence of an incubation period. However, the total capacity is lower than the cold rolled samples. Milling for 60 min is detrimental, making the sample harder to activate than the as-received sample. The reduction of capacity with milling was also reported by Joseph et al. [26,27].

In the case of cold rolling, the sample that was rolled 5 times has a short incubation time and reaches the full capacity. The samples that were rolled 12 and 25 times have longer incubation times and the sample rolled 25 times shows a reduction of capacity. Fig. 2(b) shows the first desorption for all samples. It demonstrates that desorption kinetic is intrinsically the same for all samples, the only variation being the capacity.

Fig. 3 presents the absorption/desorption curves for the second cycle. It is clear that, except for the ball milled 60 min sample, all samples have the same intrinsic kinetics, the only discrepancies being the total capacity. From these kinetics and the ones shown in Fig. 2(b), we could conclude that mechanical deformations

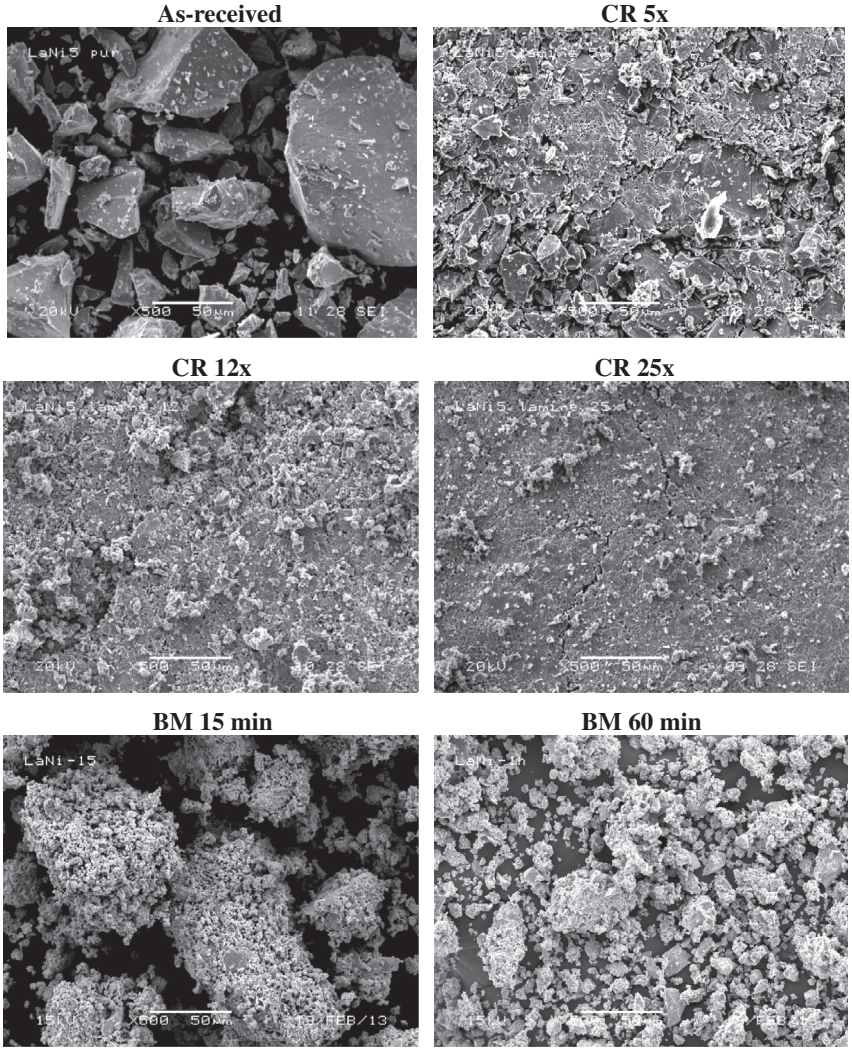

Fig. 1. Scanning electron microscope (SEM) micrographs of $LaNi_5$: as-received, cold rolled and ball milled. Magnification of 500 times for all images.