Metals **2015**, *5*, 2021-2033; doi:10.3390/met5042021

OPEN ACCESS

metals

ISSN 2075-4701
www.mdpi.com/journal/metals/

Article

Effect of Cold Rolling on the Hydrogen Desorption Behavior of Binary Metal Hydride Powders under Microwave Irradiation

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Academic Editor: Hugo F. Lopez

Received: 25 August 2015 / Accepted: 22 October 2015 / Published: 28 October 2015

Abstract: In this paper we report that cold rolling could drastically improve hydrogen desorption kinetics under microwave irradiation. Samples of metal hydride powders (TiH_2, ZrH_2, and MgH_2) in as-received conditions and after cold rolling were microwave irradiated in a vacuum using a simple experimental setup. After irradiation, the samples were characterized by X-ray diffraction in other to evaluate the effectiveness of microwave heating. The diffraction patterns indicated that only MgH_2 could be fully decomposed (dehydrided) in the as received state. TiH_2 was only partially decomposed while no decomposition was observed for ZrH_2. However, cold rolling the hydride powders prior to microwave heating led to a significant improvement of hydride decomposition, resulting in the complete dehydriding of TiH_2 and extensive dehydriding of ZrH_2. These results clearly indicated the positive effects of cold rolling on the microwave assisted desorption of the investigated binary hydrides.

Keywords: metal hydrides; microwave heating; hydrogen desorption; cold rolling; magnesium hydride; titanium hydride; zirconium hydride

1. Introduction

The use of microwave energy in material synthesis and processing has been widely investigated over the years. This approach has been successfully used in the synthesis of micrometric and nanometric particles, microwave sintering, surface modification, *etc.* [1–6]. The most investigated use of microwaves in materials processing and synthesis is the microwave sintering of oxides, carbides, nitrides, silicides, *etc.* [7].

The microwave heating of metals was considered a minor subject for a long time since the penetration depth of electromagnetic fields into metals is quite small (up to few micrometers), limiting the heating reached in bulk metals. For detailed information on the electromagnetic field interaction with metals during microwave irradiation, the interested reader may refer to the review article by Yoshikawa [8]. However, this scenario changed markedly in 1999 when Roy *et al.* [9] reported for the first time the microwave heating and sintering of a porous metal compact, extending the applicability of microwave irradiation in materials processing. Subsequently, the interest in the microwave assisted processing of metals, alloys and metal matrix composites became reality [10–13].

Nowadays, the search for clean energy sources is a major target worldwide and hydrogen appears as a promising energy vector candidate [14–16]. Conversely, a number of important technological problems must to be solved in order to allow the large scale utilization of hydrogen in practical energy systems. One of the most challenging issues to be solved is finding safe and reliable technologies for hydrogen storage. Metal hydrides are interesting materials for solid state hydrogen storage, and several hydride systems and different materials processing routes have been extensively investigated [14–24].

Despite of the abovementioned growing interest in the microwave heating of metallic materials, until now only few papers addressing the microwave irradiation in metal hydrides have been published. Luo *et al.* [25] reported that titanium sintered parts obtained by the microwave irradiation of TiH_2 showed higher densities, finer residual pores and better mechanical properties than those obtained from hydride-dehydrided titanium powder. Li *et al.* [26] employed microwave sintering to process Mg-La-Ni hydrogen storage alloys from elemental powders and successfully obtained multi-phase alloys. Microwave assisted synthesis of hydrides was also performed by Tapia-Ruiz *et al.* [3] to produce the Li_4NH hydride by solid state reaction between Li_3N and LiH compounds. This reaction is complex, presenting possible alternative pathways and side reactions with atmosphere or container material contaminations. These authors reported success in producing single phase Li_4NH by microwave synthesis over a much shorter period of time than necessary for conventional heating methods.

Hydrogen desorption promoted by microwave heating was also reported in a few papers. Nakamori *et al.* [27] investigated the effect of microwave irradiation on some metal hydrides and complex hydrides. These authors reported that some of the investigated transition metal hydrides presented small hydrogen desorption (TiH_2 and $VH_{0.81}$), as indicated by shifts in diffraction peaks positions of the hydride phases, whereas others did not indicate any hydrogen release (ZrH_2 and $LaH_{2.48}$).

Similar behavior was observed for complex hydrides, where $LiBH_4$ showed partial desorption whereas $NaBH_4$ and KBH_4 do not show any evidence of desorption by microwave irradiation. The authors concluded that microwave penetration depth and conduction losses are controlling factors on microwave heating and hydrogen desorption for the investigated hydrides. Krishnan [28] also studied the effects of microwave irradiation in $NaAlH_4$ and $TiCl_2$ doped $NaAlH_4$. The authors concluded that, when the metallic phase Al is present in the starting material, microwave exposure leads to the production of reversible Na_3AlH_6 and Al phases. However, when the sample does not contain an Al phase then microwave irradiation produces an amorphization of $NaAlH_4$. Zhang *et al.* [29] proposed the use of a Ni-coated honeycomb ceramic monolith (HCM) as susceptor to promote fast heating and hydrogen desorption in MgH_2 and other hydrides. Awad *et al.* [30] investigated the effect of different types of carbon (carbon fibers, graphite and diamond) on the hydrogen desorption behavior of Mg + C nanocomposites obtained by ball-milling and reported that more effective desorption was obtained by increasing the milling time, the carbon type content and microwave power. Among the investigated composites, the MgH_2 + 10% CF showed the larger hydrogen release, converting about 90% of the initial MgH_2 in Mg.

A possible application of the microwave desorption is for Zircaloy recycling as mentioned by Dupim *et al.* [31]. As for absorption, to our knowledge absorption under microwave radiation has not been reported yet. The reason may be the necessity of having a sample holder that has to support hydrogen pressure while being permeable to microwaves, which increases the safety issue. In the present investigation only desorption was investigated.

In this work, we investigate the effect of cold rolling on the hydrogen desorption behavior of binary hydride powders during microwave irradiation. This investigation was motivated by the reports concerning the positive effects of cold rolling on the hydrogen desorption kinetics in several hydride systems under conventional heating [31–36] and also the lack of investigations focusing the effect of cold rolling on the hydrogen desorption of hydrides during microwave heating.

2. Experimental Section

MgH_2, TiH_2, and ZrH_2 powders having respectively 98%, 99%, and 98.5% purity (metal basis), were used in microwave desorption experiments. Cold rolling was performed by placing the hydride powder between two aluminum plates and rolling it 5 times using a Durston 130 laboratory rolling mill (Durston, High Wycombe, Buckinghamshire, UK). The cold rolling was performed in air.

For microwave irradiation, a domestic microwave oven (Danby model DMW 749SS, Danby, Guelph, ON, Canada) specially adapted for these experiments was used. This microwave oven has a power of 700 W and frequency of 2.5 GHz. A quartz tube with one side dome closed and the other open (200 mm in length and 10 mm diameter) was used as sample holder and a stainless steel cylinder (diameter 0.8 mm) was used as susceptor. The open extremity of this tube was linked to a vacuum pump for dynamic evacuation during the experiments. The level of vacuum was about 10^{-2} torr. The mass of the hydride powder was about 200 mg. A schematic representation of the sample holder used for these experiments is shown in Figure 1. The investigated samples (as-received and cold-rolled) were placed into the quartz tube inside an argon filled glove-box. Irradiation experiments were performed with a fixed duration of 30 min.

The morphology of the metal hydrides was observed by scanning electron microscopy (SEM) using a Philips XL30 microscope (FEI, Hillsboro, Oregon, USA). Working distance and accelerating voltage were varied according to the operating mode of the microscope (backscattered or secondary electron). The actual values are indicated on the respective micrographs. The investigated samples were characterized by X-ray diffraction using a Bruker D8 Focus diffractometer (Cu-Kα radiation), Bruker, Madison, WI, USA. Rietveld refinement was performed using the Topas software (Bruker, Madison, WI, USA) [37].

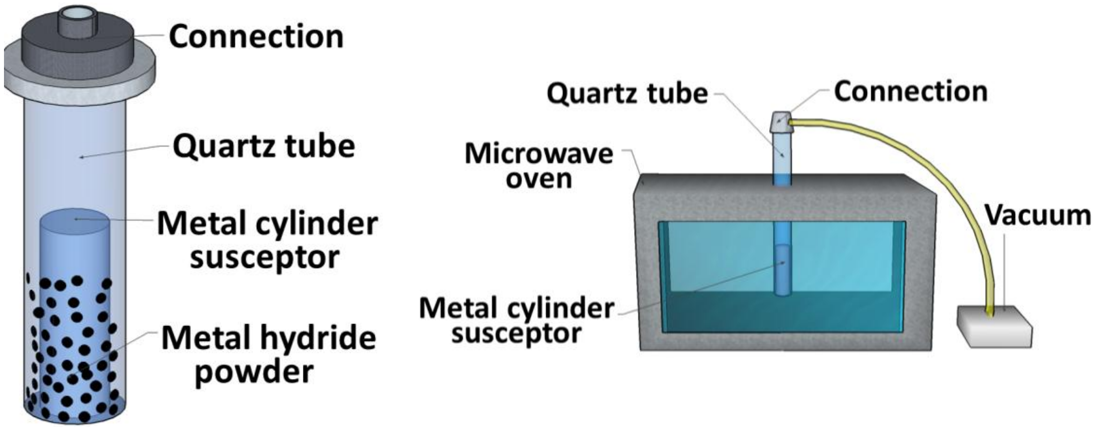

Figure 1. Schematic representation of the sample holder used for microwave irradiation experiments.

3. Results and Discussion

3.1. Electron Microscopy

Figure 2 shows the morphologies of hydride powders investigated by scanning electron microscopy images obtained with a secondary electrons detector (SE-SEM). Figure 2a–c correspond to MgH_2, TiH_2, and ZrH_2 as-received powders, respectively. It is clear that all the samples show irregular particle morphology, with relatively widespread particle sizes. Moreover, it is noticeable that ZrH_2 powder has the larger mean particle size, followed by MgH_2 and TiH_2.

The effect of cold rolling on the morphology of the hydride powders can be observed in Figure 2d–f for MgH_2, TiH_2, and ZrH_2 respectively. All the rolled samples presented a morphology of large plate-like agglomerates composed of very fine particles, with particles sizes in the range of sub-microns to few microns. The strong particle size refinement promoted by cold rolling on the hydride powders can be clearly seen. The particle size refinement is a positive feature for microwave heating since the microwave penetration depth in metals is small. Moreover, the decrease in particle size allows the metal powder to reach higher temperatures as demonstrated by Mondal *et al.* [38] in the case of microwave irradiation of Cu powder.

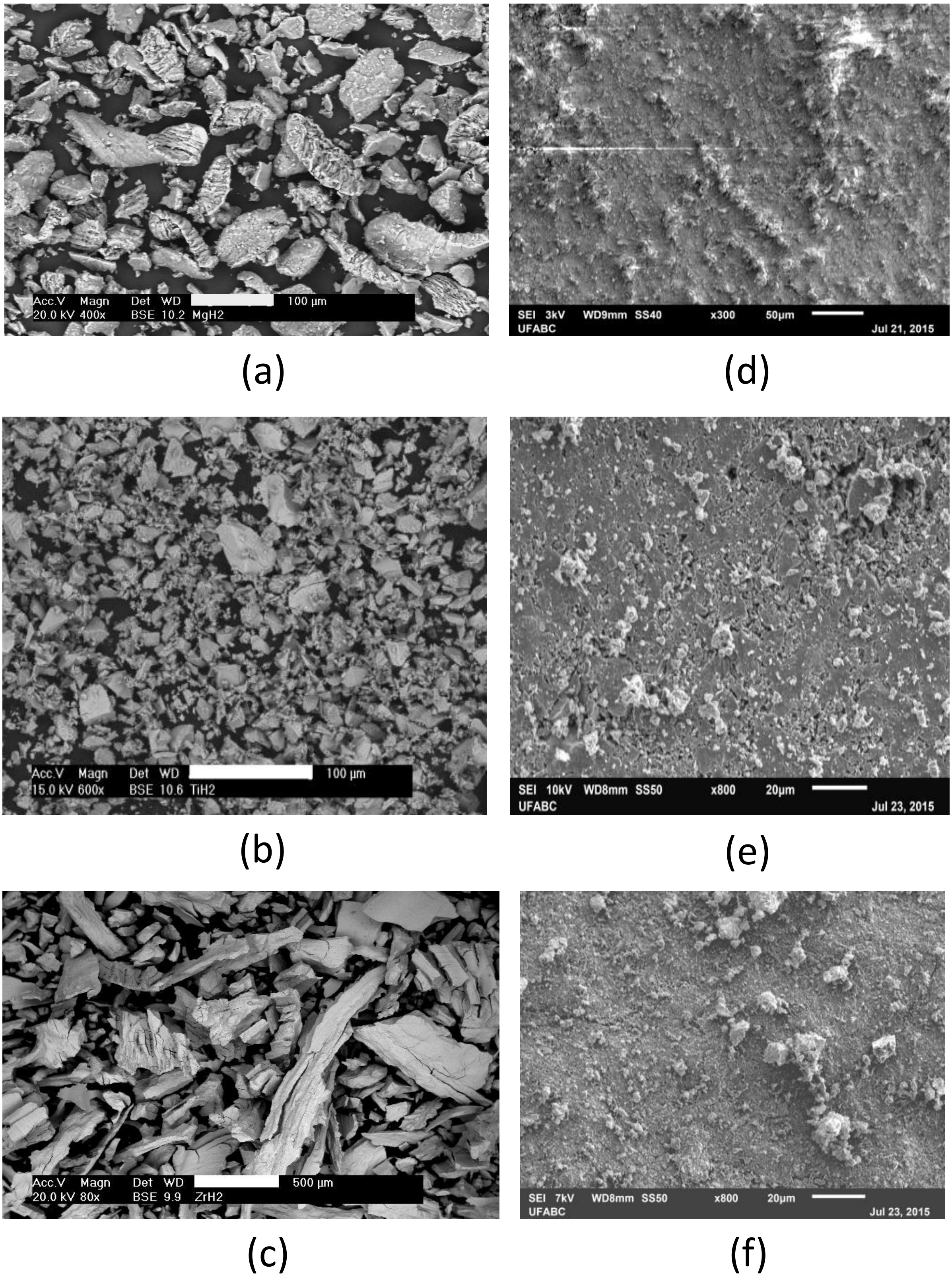

Figure 2. Morphology of metal hydride powders observed by scanning electron microscopy (SEM). Images (**a**), (**b**), and (**c**) correspond to as-received MgH_2, TiH_2, and ZrH_2, respectively, whereas (**d**), (**e**), and (**f**) correspond to coldrolled MgH_2, TiH_2, and ZrH_2, respectively.

3.2. X-ray Diffraction: Cold Rolling Effects

The X-ray diffraction (XRD) patterns of as-received and cold rolled samples of MgH_2, TiH_2, and ZrH_2 are shown in Figures 3–5, respectively.

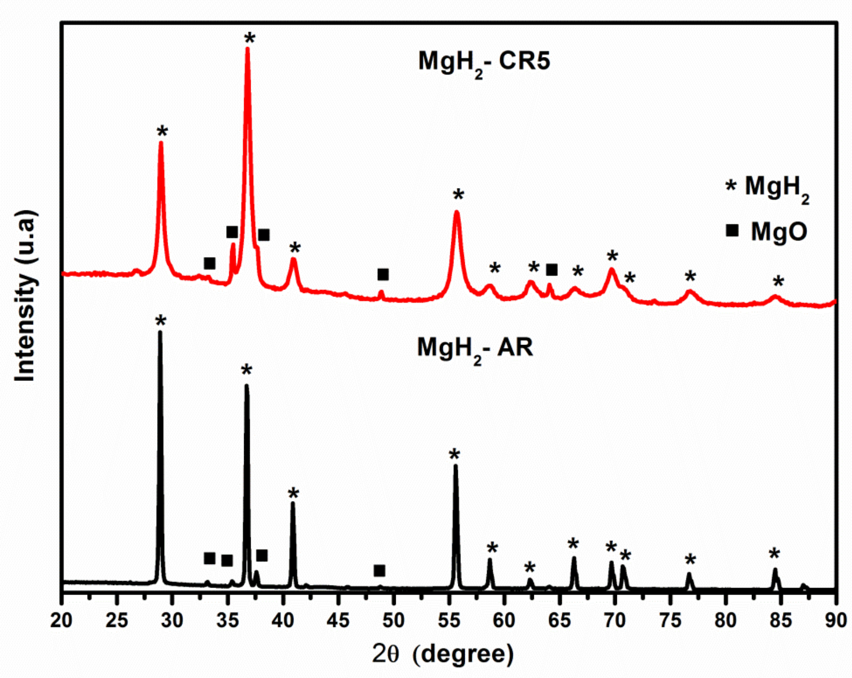

Figure 3. X-ray diffraction patterns of as-received and cold rolled (5 passes) MgH_2 powders. (CR): cold rolled; (AR): as-received.

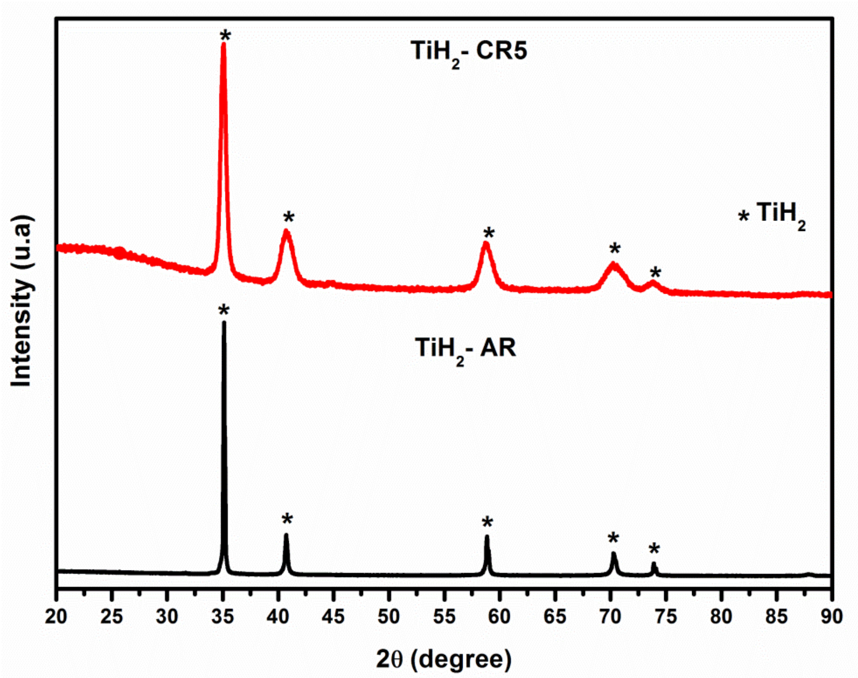

Figure 4. X-ray diffraction patterns of as-received and cold rolled (5 passes) TiH_2 powders.

The XRD patterns of MgH_2 shown in Figure 3 indicate the predominance of the hydride phase with some observable peaks of magnesium. Cold rolling caused broadening of the diffraction peaks which can be ascribed to lattice defects and crystallite size reduction. A quantitative analysis performed using Rietveld refinement indicated the same amount of Mg and MgH_2 in the as-received and cold rolled samples. However, the crystallite size was greatly reduced by cold rolling, going from 114 nm in the as-received sample to 14 nm in the cold rolled sample.

In the case of TiH_2, the X-ray patterns presented in Figure 4 indicate that cold rolling greatly broadened the Braggs peaks. However, contrary to the results found with MgH_2 where the broadening was due to reduction of crystallite size, here the crystallite size remains essentially constant (60 nm) but the microstrain is increased by an order of magnitude from 0.02% in the as-received sample to 0.4% in the cold rolled sample.

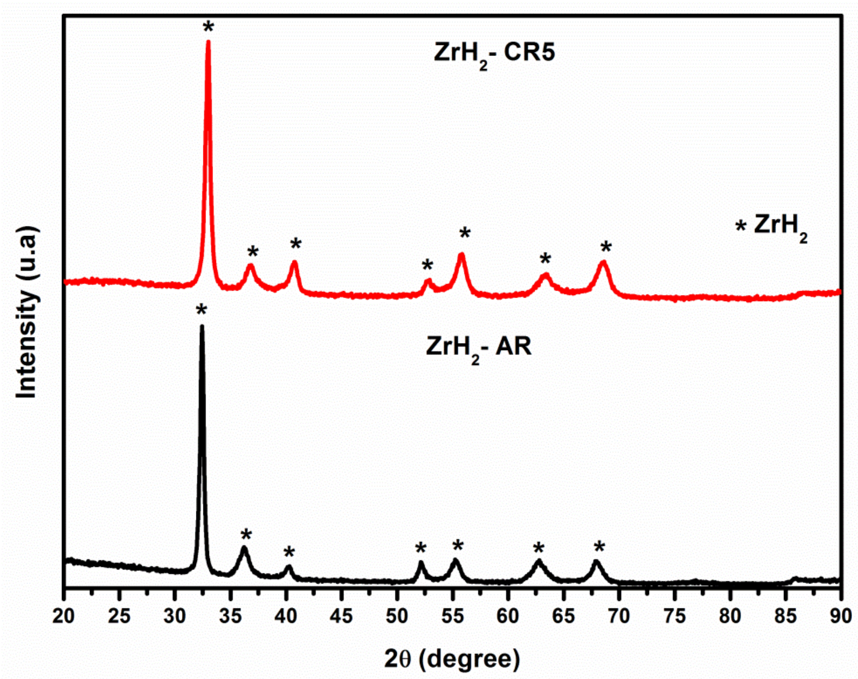

Figure 5. X-ray diffraction patterns of as-received and cold rolled (5 passes) ZrH_2 powders.

As shown in Figure 5, the X-ray patterns indicate that, in ZrH_2 sample, no other phases are present beside the hydride phase. It should be noticed that the peak broadening induced by cold rolling is not as important as for MgH_2 and TiH_2. In fact, Rietveld analysis indicated that, comparing as-received and cold rolled samples, the crystallite size goes from 29 nm to 20 nm while the microstrain goes from 0.2% to 0.3%.

3.3. X-ray Diffraction: Microwave Irradiation Effects

The X-ray diffraction patterns of as-received and cold rolled samples after microwave irradiation of MgH_2, TiH_2, and ZrH_2 are shown in Figures 6–8, respectively. In the case of MgH_2 (Figure 6), both as-received and cold rolled samples were fully dehydrided by microwave irradiation. Nakamori *et al.* [27] investigated the effect of microwave irradiation in several hydrides and reported the ineffectiveness of that technique for desorption of MgH_2. In their case, the results may be explained by the limited increases of temperature they recorded. However, for ZrH_2 and TiH_2 relatively high temperatures were reached (more than 700 K and 800 K, respectively) and minimal hydrogen desorption was recorded. Therefore, the microwave heating and resulting dehydriding observed in our experiment might be ascribed to the use of a microwave susceptor (metallic cylinder). In our work, the metallic cylinder used as susceptor ensured a close contact with the hydride powder which remained confined between the susceptor and the sample holder wall ensuring an effective heating of the hydride powder. The efficiency on the use of susceptors for microwave irradiation and hydrogen desorption in MgH_2 was demonstrated by Zhang *et al.* [29] who designed a honeycomb ceramic monolith susceptor for this purpose. Awad *et al.* [30] prepared MgH_2 composites adding different types of carbon compounds (carbon fiber, graphite, and diamond, which are good microwave absorbers) during ball-milling and observed the effectiveness of this approach in increasing the hydride decomposition during irradiation.

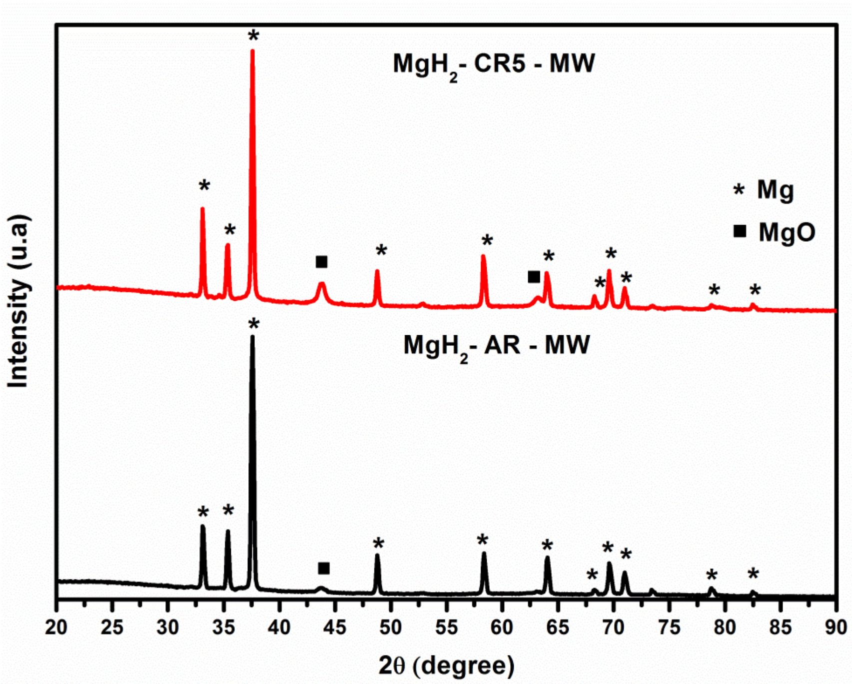

Figure 6. X-ray diffraction patterns of as-received and cold rolled (5 passes) MgH_2 powders after microwave irradiation.

The XRD patterns of TiH_2 samples after microwave irradiation are shown in Figure 7. In both samples (as-received and cold rolled), the hydride decomposition was not complete. The positive effect of cold rolling on the hydrogen desorption is clear from the relative intensities of the diffraction peaks of hydrides and Ti metal phases. From Rietveld refinement we found that, after microwave irradiation, the as-received sample was made of 93 wt.% of titanium hydride (TiH_2 and $TiH_{1.5}$) and only 7 wt.% of titanium. In the case of cold rolled sample, after microwave irradiation the proportion of TiH_2 was 46 wt.%, the rest being titanium.

Nakamori *et al.* [27] highlighted that TiH_2 is suitable for microwave heating (microwave absorber) but showed limited hydrogen desorption. This behavior was ascribed to a limited electromagnetic penetration depth in TiH_2, deduced by these authors as 11 μm for their experimental condition, leading to hydride decomposition only close to the surface. In our work, the hydrogen desorption from the TiH_2

sample was much higher than that reported in Nakamori's work. These results demonstrated the improvement in hydrogen desorption from TiH_2 promoted by cold rolling.

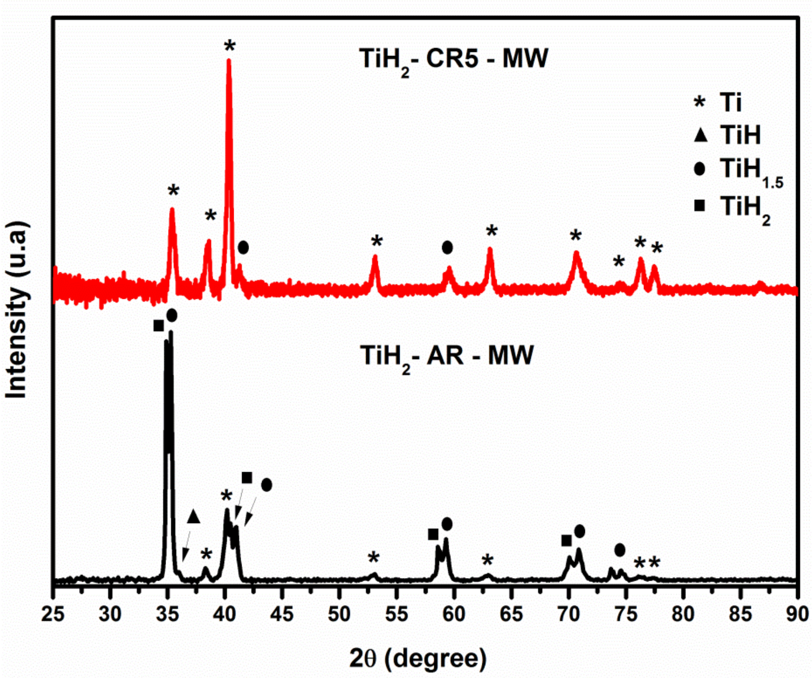

Figure 7. X-ray diffraction patterns of as-received and cold rolled (5 passes) TiH_2 powders after microwave irradiation.

Cold rolling was most effective in the case of ZrH_2. As shown in Figure 8, the pattern for the as-received sample display only peaks during to the hydride phase which means that microwave heating was totally ineffective. On the contrary, the pattern of the cold rolled sample did not show any ZrH_2 peaks but instead only showed peaks that could be indexed to the Zr metal phase and zirconium oxide. Considering the high thermodynamic stability of ZrH_2, the obtained result is very interesting and may open new possibilities for fast hydride and dehydride Zr and its alloys, which is an interesting topic in several areas, such as the nuclear industry.

As for TiH_2, the absence of dehydrogenation for the as-received sample may be due to by the small electromagnetic field penetration depth in Zr and the high thermodynamic stability of the ZrH_2 phase which prevented the hydride decomposition. By cold rolling, the particle size is reduced and defects are generated which contribute positively to the effectivity of microwave heating. Concerning the positive effect of cold rolling on hydrogen desorption, similar behavior has been observed for the conventional heating of cold rolled hydride powders [31,39,40]. This behavior has been attributed to the decrease in crystallite size and crystal defects generated during rolling which could act as fast diffusion paths and heterogeneous nucleating sites for diffusional phase transformations. Similar behavior may be expected for microwave heating. Particularly concerning ZrH_2, beneficial effect of cold rolling for improving the hydrogen desorption kinetics in conventionally heated ZrH_2 was reported in our previous investigation on the hydriding and dehydriding behavior of Zircaloy chips [32].

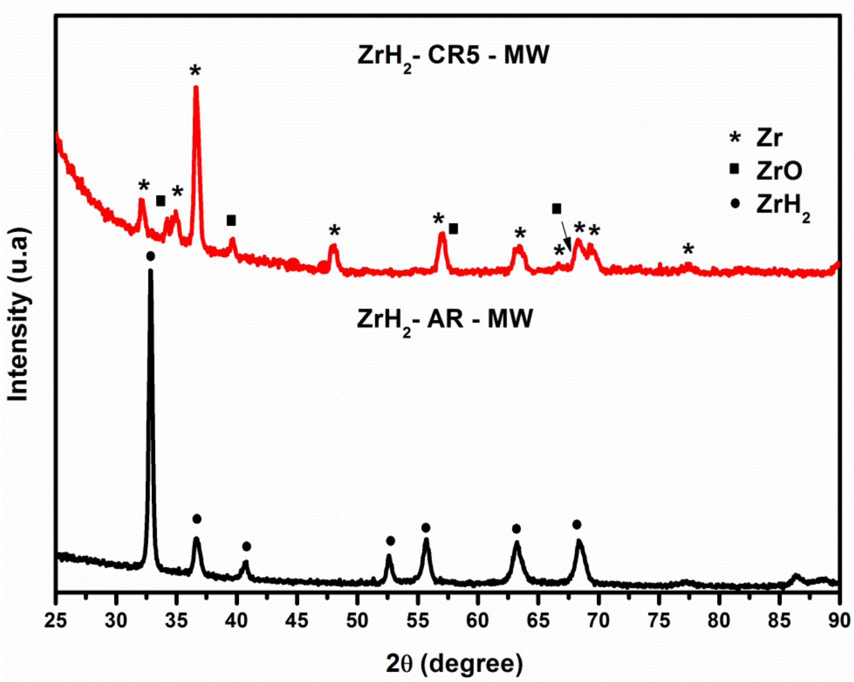

Figure 8. X-ray diffraction patterns of as-received and cold rolled (5 passes) ZrH_2 powders after microwave irradiation.

It should be noticed that after microwave irradiation in a few cases there was formation of oxides while in other cases no oxides were formed. For example, MgH_2 in as-received and cold rolled states presented formation of oxides after microwave irradiation while for TiH_2 no oxides were formed. The explanation may be that when a hydride phase subsisted, it prevented oxidation of the material. As a proof we see that for ZrH_2 the as-received sample after microwave irradiation did not desorbed at all and there were no oxides formed while the cold rolled sample fully desorbed and there is the presence of zirconium oxide.

From these experiments and by comparing with the results of Nakamori *et al.* [27], it is clear that the use of a susceptor greatly improved the effectiveness of microwave irradiation. A critical measurement that is missing in this investigation is the temperature during the reaction. This lack of recording temperature was due to the interaction between microwave and thermocouple. We are planning to solve this problem in a future investigation. Nevertheless, as MgH_2 decomposed to magnesium powder after microwave irradiation, we know that melting temperature was not reached, which means that in our experiments the temperature reached was probably not so different than in Nakamori's case.

4. Conclusions

Microwave irradiation in binary metal hydrides was investigated. In the case of MgH_2 the feasibility of microwave heating was observed and its complete dehydriding was made possible by using a susceptor in a simple experimental setup. Despite the low penetration depth of the electromagnetic field in TiH_2, previously reported in the literature, extensive desorption was achieved after cold rolling this hydride powder. As ZrH_2 is much more stable than TiH_2, decomposition of as-received ZrH_2 was even more difficult than TiH_2 under our experimental conditions. On the other hand, full desorption of ZrH_2 was reached after cold rolling this sample. Therefore, for both TiH_2 and ZrH_2 cold rolling of the hydride powders was shown to be a feasible approach for improving the hydrogen desorption. The beneficial effect of cold rolling on the hydride decomposition is attributed to a combination of microstructural and morphological changes promoted by this processing route, which comprises particle size reduction, crystallite size reduction, and increase of residual stress. In the case of particle size reduction, this allows a more effective heating of the particles by approximating the size of the particles to the penetration depth of the electromagnetic field in metallic powders. Moreover, residual stress and crystallite size reduction can increase the number on nucleation sites and accelerate hydrogen diffusivity contributing to effective hydrogen desorption from the hydride powders.

Acknowledgments

ISD acknowledges the fellowship from the "Programme des Futurs Leaders dans les Ameriques (PFLA)" which is managed by the "Bureau Canadien de l'Education Internationale (BCEI)", Canada. SFS acknowledges FAPESP for visiting researcher fellowship (Grant 14/06127-5) and CNPq grants (558112/2010-2; 461034/2014-0; and 309202/2014-0).

Author Contributions

ISD carried out the experimental activities. ISD, SFS, and JH performed the data analysis. SFS and JH wrote the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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