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Mechanical alloying and hydrogen storage properties of $CaNi_5$-based alloys

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Abstract

$CaNi_5$-based hydrogen storage materials have been synthesized by mechanical alloying of the elemental Ca and Ni powder blend, followed by an isothermal annealing. It was found that high energy ball milling of a Ca and Ni blend does not result in the formation of the $CaNi_5$ intermetallic compound. However, DSC measurements show that the $CaNi_5$ phase forms upon heating the mechanically milled powders to 395°C. Replacement of Ca by Ce or Mm (Mischmetal), and of Ni by Zn leads to direct formation of nanocrystalline alloy phases with $CaCu_5$ structure. The as-milled nanocrystalline powder does not absorb much hydrogen. A post-milling isothermal annealing at 640°C leads to grain growth and release of microstrain, and to an improvement of the hydrogen storage properties. Replacement of Ca by Ce or Mm increases the plateau pressure, while replacement of Ni by Zn reduces the desorption plateau pressure.

Keywords: Mechanical alloying; Nanostructures; Hydrogen absorbing alloys; $CaNi_5$

1. Introduction

The $CaNi_5$ intermetallic represents a category of low cost hydrogen storage materials with a storage capacity up to 1.9 wt.% [1–3]. However, little attention has been paid to this system, probably due to its bad cycling stability [4]. Improvement of the hydrogen storage properties of $CaNi_5$ by replacement of Ca or Ni by third elements has been tried [5,6]. However, the substitution behavior and hydrogen storage properties of the modified compounds are still not well understood.

Traditionally, $CaNi_5$ was synthesized by casting [1–5]. Since Ca does not form alloys with most early transition metals and rare earth metals [7], it is very difficult to make substituted $CaNi_5$ alloys containing these elements. In addition, some alloying elements such as Zn and Sn, have very low melting point in comparison with Ca, Ni and their compounds, so casting substituted $CaNi_5$ alloys containing Zn and Sn is also difficult.

Mechanical alloying can achieve atomic level homogeneous alloying and extended solid solutions at room temperature, and has been widely used to synthesize new alloys [8]. Moreover, low cost Ca turnings and granules are available, and are well suited for mechanical alloying applications. Therefore, the syntheses of $CaNi_5$ based alloys by mechanical alloying is of technical interest. In this paper, we have synthesized $CaNi_5$ and substituted $CaNi_5$-type alloys by mechanical alloying followed by isothermal annealing. The hydrogen storage properties of these alloys were investigated.

2. Experimental

The mechanical alloying was done by using a Spex 8000 ball mill. The calcium particles (1–2 mm in diameter) from Timminco, and nickel and zinc powders purchased from Alfa were used as raw materials. Mm and Ce powders were made inside a glove-box by pulverizing the ingots (from Aldrich) under the protection of argon. The mischmetal Mm contains 51%Ce, 26.4%La, 16.4% Nd and 5.3%Pr (in wt.%).

The powders were mixed in the desired composition and mechanically milled in a steel milling vial filled with argon. Three steel balls of diameter 11 mm were used. The ball to powders mass ratio was 10:1.

The post-milling isothermal annealing was done under a vacuum better than 10^{-4} torr. The hydrogen storage properties were evaluated by using an automated Sieverts

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apparatus. The X-ray powder diffraction was performed on a Siemens D500 apparatus with CuKα radiation. The lattice parameters were determined from diffraction peak positions. The crystallite size was evaluated from the broadening of X-ray diffraction (XRD) peaks using the Williamson–Hall method [9]. The peak position and peak broadening were calibrated by using strain free pure Si powders. The differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC7 apparatus at a scanning rate of 20°C/min. The powder was protected by N_2 flow during DSC measurement.

3. Results and discussion

3.1. Mechanical alloying

Fig. 1 shows the XRD spectra of the $CaNi_5$ powder blend mechanically alloyed for various times. After 0.2 h of mechanical milling, the Ca and Ni peaks can be clearly seen. The intensity of Ca peaks is small due to its low proportion. After 1 h of milling, all the calcium and nickel powders stick to the steel vial and balls. By increasing the milling times to 5 h, the Ca–Ni coatings on the balls and the wall of the crucible break, and a fine powder is obtained.

The Ca peaks disappear and the diffraction peaks of the $CaNi_3$ phase appear in the powder subjected to 2 h of mechanical alloying. Increasing the milling time to 10, 20, 40 and 70 h does not lead to the formation of the $CaNi_5$ phase. The nickel peaks are still present after 70 h of milling. The peak position of Ni does not change. A strong halo arises in the range of $30° < 2\theta < 55°$, probably due to partial amorphization. The $CaNi_3$ phase is perhaps still present after 70 h of milling, its diffraction peaks are buried in the high background.

The 70 h milled powder was subjected to a DSC measurement in order to see at what temperature the formation of $CaNi_5$ takes place. A scan up to 640°C leads to an exothermic reaction with a peak temperature of 395.5°C, as shown in the insert of Fig. 1. The exothermic reaction enthalpy was calculated to be −71.2 J/g, or −4.2 kJ/mol·atom, which is about 2/3 of the calculated formation enthalpy of the $CaNi_5$ phase. This measurement indirectly indicates that some alloying reaction between Ca and Ni had taken place during mechanical milling. The powder was rapidly cooled to room temperature after being heated to 640°C. XRD analysis of the DSC measured powder shows the formation of the $CaNi_5$ phase.

Partial substitution Ce or Mm for Ca leads to the direct formation of the $Ca_{0.9}Ce_{0.1}Ni_5$ and $Ca_xMm_{1-x}Ni_5$ ($x=0.15, 0.2$) phases with $CaCu_5$ structure. Substitution of Zn for Ni leads to similar results. Fig. 2 shows the XRD spectra of various substituted $CaNi_5$ type alloys. The mechanically alloyed Mm- and Zn-substituted $CaNi_5$ type phases have very small grain size, indicated by their very broad XRD peaks. The grain size and microstrain of the

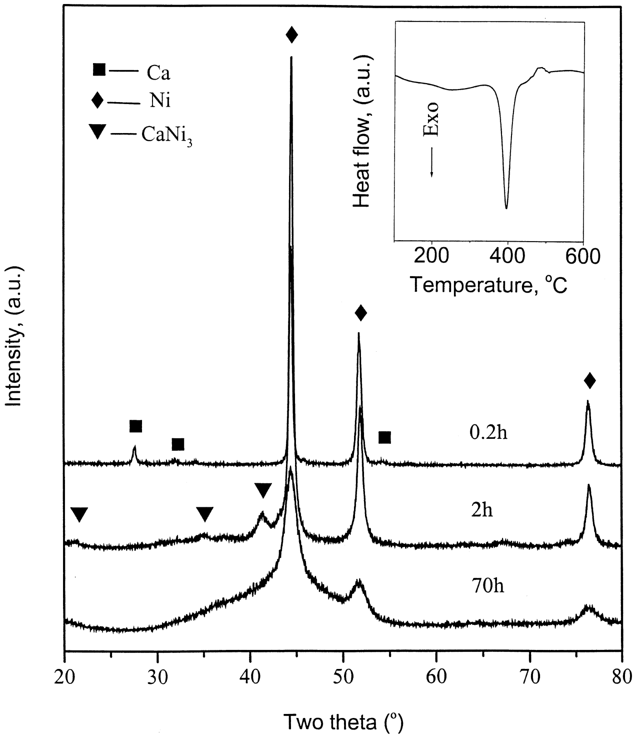

Fig. 1. XRD spectra of the $CaNi_5$ powder blends mechanically milled for various times, and the insert DSC curve of the mechanically alloyed $CaNi_5$ (70 h).

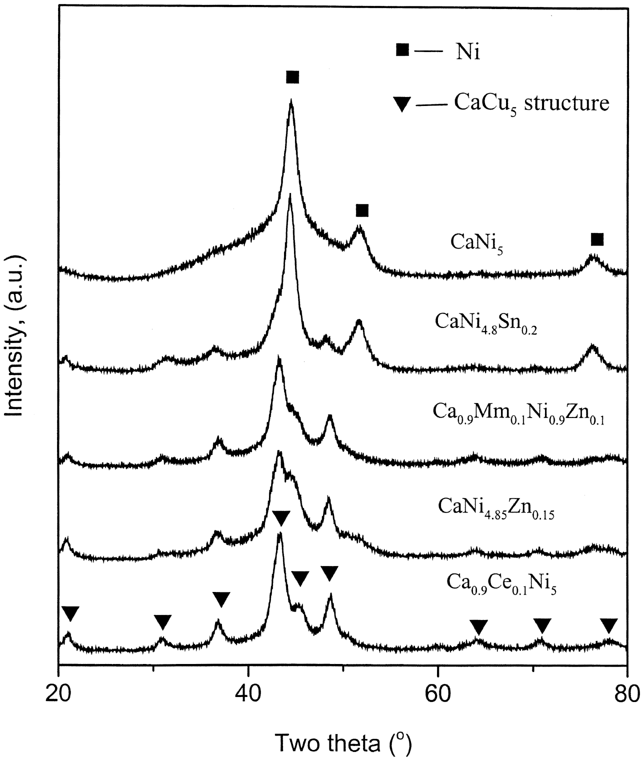

Fig. 2. XRD spectra of various mechanically alloyed powders.

mechanically alloyed $Ca_{0.9}Ce_{0.1}Ni_5$ were determined to be 8±1 nm and 0.51±0.06%, respectively.

The replacement of Ca by Ce or Mm and Ni by Zn probably increases the reaction enthalpy of the compounds. Therefore, the driving force for alloying the elemental components is bigger, and as a result, the $CaNi_5$-type phase forms during mechanical milling.

Tin substitution for Ni leads to partial formation of the $CaNi_5$-type phase. The strong Ni peaks are still present on the XRD spectrum of the $CaNi_{4.8}Sn_{0.2}$ after 40 h of milling (see Fig. 2). The peak positions of this $CaNi_5$-like phase are shifted to low angles, indicating that the lattice parameters are increased. Only a very small exothermic reaction peak is observed in the DSC trace of this compound (not shown). This DSC peak is not related to the formation of $CaNi_5$, since the $CaNi_5$ type phase disappeared after annealing and a new unidentified phase is observed. The XRD spectrum of this DSC measured powder is similar to that of the powder after annealing (2 h at 640°C) shown in Fig. 3. The sharp XRD peaks indicate that the grain growth and release of microstrain have taken place. For the case of $Ca_{0.9}Ce_{0.1}Ni_5$, the grain size and microstrain were measured to be 34±2 nm and 0.11±0.02%, respectively, after annealing.

3.2. Hydrogen absorption/desorption properties

The as-milled (70 h) $CaNi_5$ absorbs 0.4 wt.% hydrogen at 25°C without any previous activation. However, only 0.2 wt.% can be desorbed at this temperature under vacuum. This reversible amount of hydrogen may be stored in the amorphous like phase. The rest of the hydrogen can only be released by heating to above 400°C. This amount of hydrogen may be stored in the unreacted Ca. Upon heating to 400°C, the reaction of CaH_2 with Ni takes place, $CaNi_5$ is formed and the H_2 is released.

In the case of Sn-substituted $CaNi_{4.8}Sn_{0.2}$ alloy, a small amount of hydrogen (0.25 wt.%) is absorbed by the as-milled powders. Only 0.1 wt.% is released at room temperature, the rest comes off at high temperatures (>450°C). After high temperature heat treatment, this compound does not absorb hydrogen on subsequent exposure to hydrogen, due to the formation of the new phase. The AB_5 structure disappeared upon annealing in this case.

The Ce, Mm or Zn substituted $CaNi_5$-type alloy powders prepared by mechanical alloying can reversibly absorb and desorb hydrogen in the as-prepared state without any activation treatment. However the storage capacity is small. Only 0.45 wt.% hydrogen can be reversibly stored in the as-milled $Ca_{0.9}Ce_{0.1}Ni_5$. Annealing at high temperatures improves the storage capacity. Fig. 4 shows the hydrogen absorption and desorption curves of the $Ca_{0.9}Ce_{0.1}Ni_5$ alloy powders as-milled and after annealing. The reversible hydrogen storage capacity is increased from 0.45 wt.% for the as-milled powder to about 1.2 wt.% for the annealed (640°C for 2 h) powder.

The PCI (pressure–composition isotherm) curves of the annealed pure $CaNi_5$ powder are shown in Fig. 5. The plateau pressures are comparable to those of $CaNi_5$ produced by the casting method [1]. However, only two

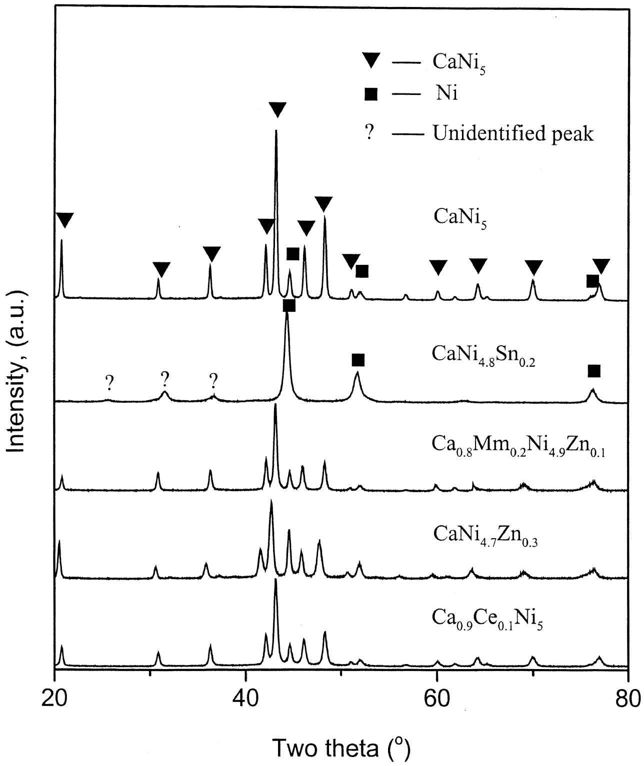

Fig. 3. XRD spectra of the substituted alloys after annealing (at 640°C for 2 h).

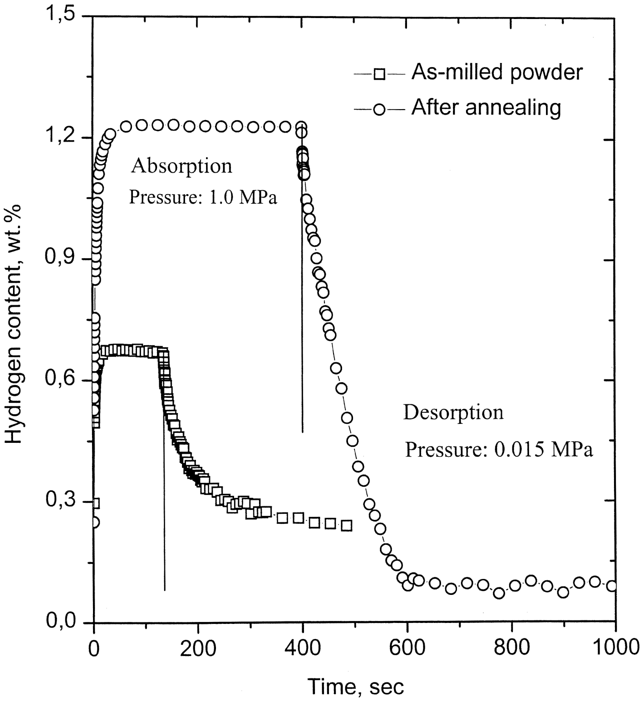

Fig. 4. Hydrogen absorption/desorption curves (at 30°C) of the $Ca_{0.9}Ce_{0.1}Ni_5$ powders as-milled and after annealing (at 640°C for 2 h).

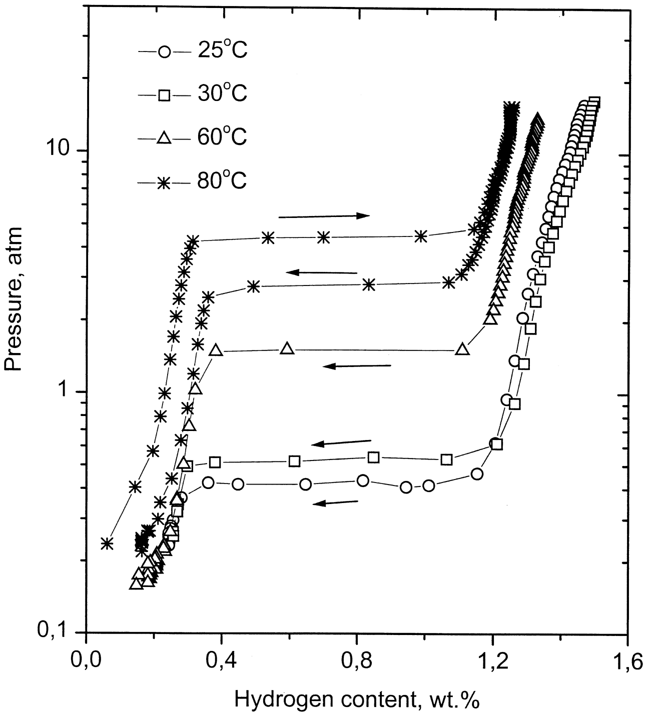

Fig. 5. PCI curves of the $CaNi_5$ prepared by mechanical alloying and annealing at 640°C for 2 h.

plateaus are observed. The lower pressure sloping plateau is in the range of H/M=0.05 to 0.3 wt.%. The second plateau starts at H/M=0.35 and ends at 1.25 wt.%. The third plateau at high pressure observed for pure $CaNi_5$ [1] is not reached in the present PCI measurements. The hysteresis of the second plateau is bigger than that of cast alloy. Similar increase of hysteresis was observed in the ball milled $LaNi_5$ system [10]. The reason for this change is unknown.

Replacement of Ca and Ni by third elements leads to a change of the unit cell volume, and to a change in the plateau pressure. The lattice parameters and plateau pressures of several $CaNi_5$ type substituted alloys are given in Table 1. Zn substitution for Ni leads to a bigger unit cell volume and to a decrease of the plateau pressure. The Ce and Mm substitutions for Ca increase the plateau pressure. Fig. 6 shows the desorption part of the PCI curves of various substituted $CaNi_5$ alloys. The plateau region is fairly flat for all alloys and that alloying makes the plateau region narrower.

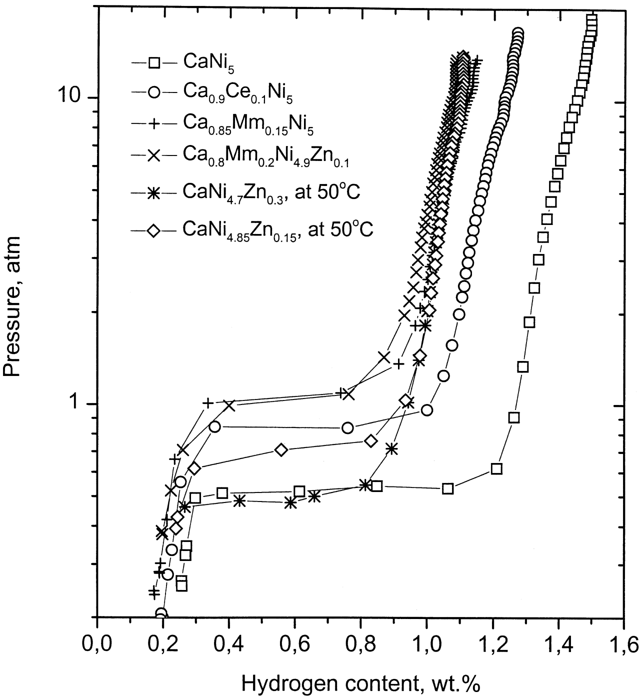

Fig. 6. PCI curves (desorption) of various substituted $CaNi_5$ alloys at 30°C.

The Mm substituted $CaNi_5$ type alloys prepared by melt-casting show much bigger slope due to the segregation of Ca and Mm during solidification. The plateaux can be flattened to some extent by homogenization annealing, but this process has its limits because of the Ca evaporation that occurs during annealing at high temperatures. It was found that a thick depleted zone forms on the surface of samples, leading to extensive precipitation of Ni during annealings at 1100°C [2].

4. Conclusions

1. Mechanical alloying of Ca and Ni powder blend does not lead to the direct formation of the $CaNi_5$ phase. A post-milling isothermal annealing is needed to obtain the $CaNi_5$ phase. The $CaNi_5$ alloys produced by

Table 1
Lattice parameters and hydrogen storage properties of several $CaNi_5$-based alloys

Alloys	Lattice parameters (Å)		Cell volume V (Å^3)	Hydrogen storage capacity (wt.%)	Desorption plateau pressure P_d (bar)	ΔH (kJ/mol)	ΔS (J/mol·K)
	a	c					
$CaNi_5$	4.9538	3.9297	83.5	1.50	0.43 at 25°C	−31.0±0.8	98.8±4.2
$Ca_{0.9}Ce_{0.1}Ni_5$	4.9529	3.9358	83.6	1.30	0.88 at 30°C	–	–
$Ca_{0.85}Mm_{0.15}Ni_5$	–	–	–	1.18	0.93 at 25°C	−29.3±1.8	99.0±5.7
$CaNi_{4.7}Zn_{0.3}$	5.0165	3.9545	86.2	1.12	0.48 at 50°C	–	–
$CaNi_{4.85}Zn_{0.15}$	–	–	–	1.10	0.71 at 50°C	–	–
$CaNi_{4.8}Sn_{0.2}$	–	–	–	0	–	–	–
$Ca_{0.8}Mm_{0.2}Ni_{4.9}Zn_{0.1}$	4.9507	3.9463	83.8	1.10	1.08 at 30°C	–	–

mechanical alloying and annealing show similar structure and plateau pressure as those of cast alloys.

2. Replacement of Ca by Ce, Mm, and Ni by Zn resulted in the direct formation of the $CaNi_5$ type phase by mechanical alloying. The reversible hydrogen storage capacities of the as-milled nanocrystalline alloys are small. Annealing gives rise to grain growth, release of microstrain, and to an improvement of the hydrogen storage capacities.
3. Replacement of Ca by Ce, Mm and Ni by Zn leads to a change of the unit cell volume, and as a result, the plateau pressure and thermodynamic properties are altered. Mechanical alloying followed by annealing at intermediate temperatures gives rise to properties similar to those obtained in cast alloys.
4. Sn can substitute for Ni to form a substituted $CaNi_5$ phase with an enlarged unit cell volume during the mechanical alloying of $CaNi_{4.8}Sn_{0.2}$. However, this $CaNi_5$ phase disappeared after high temperature heat treatment. A new unidentified phase is formed. The new phase does not absorb hydrogen under the present experimental conditions.

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