

Hydrogen absorption and desorption by $\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ powders prepared by mechanical alloying

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Abstract

$\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ elemental powder ($0 \leq x \leq 20$) mixtures were mechanically alloyed by a planetary ball mill, and phase variations after mechanical alloying (MA) and subsequent hydrogenation by gas phase loading at temperatures of 373 and 503 K, and their hydrogen desorption were investigated. The MA led to the formation of the Mg_2Ni -type phase for all powders. All powders containing Ca were induced to form an amorphous-like phase after hydrogenation at 373 K for 168 h, although the binary $\text{Mg}_{67}\text{Ni}_{33}$ powder was the α -phase ($\text{Mg}_2\text{NiH}_{0.3}$ hydride). After hydrogenation at 503 K, on the other hand, the low temperature (LT)-phase (Mg_2NiH_4 hydride) formed for all powders. The ternary powders also formed the CaH_2 hydrides. The temperature for the maximum hydrogen desorption rate increased with increasing Ca concentration in the powders after hydrogenation at both temperatures. The activation energies for hydrogen desorption for the binary powder after hydrogenation at 373 and 503 K were the same, about 92 J mol^{-1} , and those for $\text{Mg}_{47}\text{Ni}_{33}\text{Ca}_{20}$ powder at 373 and 503 K were about 168 and 244 J mol^{-1} , respectively, indicating that substitution of Ca for Mg stabilized the hydrides.

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1. Introduction

Among the available metal hydrides, Mg-based hydrides seem most promising for hydrogen storage applications because of their low cost and availability. However, the Mg-based hydride, such as Mg_2NiH_4 , is too stable and hydrogen desorption is very slow at room temperature, limiting their actual applications. The substitution of constituent elements (Mg and Ni) for other elements and/or altering the structures of the alloys, by mechanical alloying (MA), for instance, can change stability of the metal hydrides [1]. Ca–Ni based alloys, on the other hand, are also low-cost hydrogen storage alloys, and the substitution of Mg for Ca [2], in the CaNi_5 , for instance, or quaternary alloys of MgCaNi_4 alloys [3] had been attempted to improve the hydrogen storage properties. The maximum absorption concentration of hydrogen for an amorphous $\text{Mg}_{62}\text{Ni}_{33}\text{Ca}_5$ alloy, produced by melt-spun, had been reported to reach 2.3 mass% at 323 K [4]. In this paper,

$\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ elemental powder mixtures were mechanically alloyed in the Ca concentration range between 0 and 20 at.%, and the substitution of Ca for Mg while keeping Ni concentration constant in the Mg_2Ni structure by MA was attempted. The phase variations after mechanical alloying and subsequent hydrogenation by gas phase loading at temperatures of 373 and 503 K, and their hydrogen desorption were also investigated.

2. Experimental procedure

Commercially pure Mg (99.9%, –20 mesh) and Ni (99.9%, –100 mesh) elemental powders, and Ca (99%, 0.5–5 mm in diameter) granules were used as starting materials in this study. The elemental mixtures with a chemical composition of $\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ ($0 \leq x \leq 20$) were poured into stainless-steel vials, which also contained stainless-steel balls. The ball-to-mixture weight ratio was approximately 8:1. The vials containing the elemental mixture and the balls were evacuated by a rotary-pump and then back-filled with

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an argon gas (99.9999%) several times in a glove box, and the final argon gas pressure was kept to be 0.1 MPa. MA was carried out in a Fritsch Pulverisette 7 planetary ball mill. The ball acceleration was $15 \times g$. To avoid any temperature increases during MA, the alloying period of 0.25 h was alternated with an equal rest time. The high-pressure hydrogenation was performed at temperatures of 373 and 503 K by using a high-pressure vessel made of a stainless-steel. The initial hydrogen pressure was 3.5–5 MPa. Powder X-ray diffraction (XRD) measurements were made with Cu $K\alpha$ radiation to identify the phases before and after hydrogenation. Differential scanning calorimetric (DSC) analyses were also performed for the hydrogenated powders by a Shimadzu DSC-60 under an argon gas flow.

3. Results and discussion

Fig. 1 shows XRD patterns for the $Mg_{67-x}Ca_xNi_{33}$ mixtures after MA for 45 h. The elemental powders were well mixed, and the X-ray intensities were totally decreased at an early stage of MA. After MA for about 15 h, the broad peaks corresponding to the Mg_2Ni -type phase (hexagonal structure) appeared. Thus, the MA process induces the formation of the Mg_2Ni -type phase for all mixtures, although a melt-spun technique had reported to produce an amorphous phase by adding 5–20 at.% Ca to Mg–Ni binary alloys [5]. Ca seems to be mixed completely in ternary mixtures, but the small amount of Ni still remains even after MA for 45 h. The CaO oxide is also observed in the Ca-rich mixture, particularly for the $Mg_{47}Ni_{33}Ca_{20}$ powder. The c/a ratio of the lattice parameters of the Mg_2Ni -type phase increased up to approximately 4% with increasing Ca concentration in the mixtures, indicating that some of the original Mg sites in the crystal lattice became occupied by Ca atoms.

XRD patterns for the $Mg_{67-x}Ca_xNi_{33}$ mixtures after hydrogenation for 168 h at a temperature of 373 K and

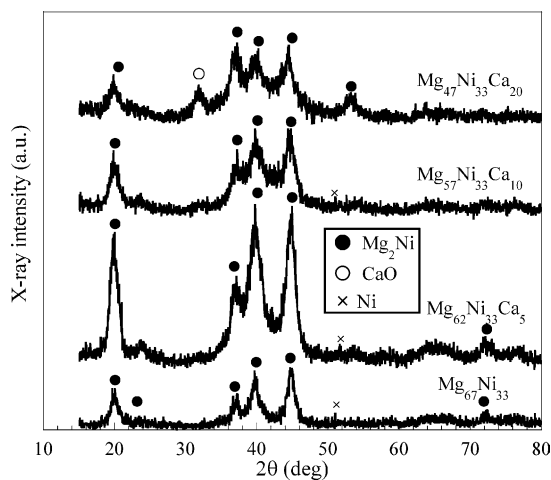


Fig. 1. X-ray diffraction patterns for the $Mg_{67-x}Ca_xNi_{33}$ mixtures after mechanical alloying for 45 h.

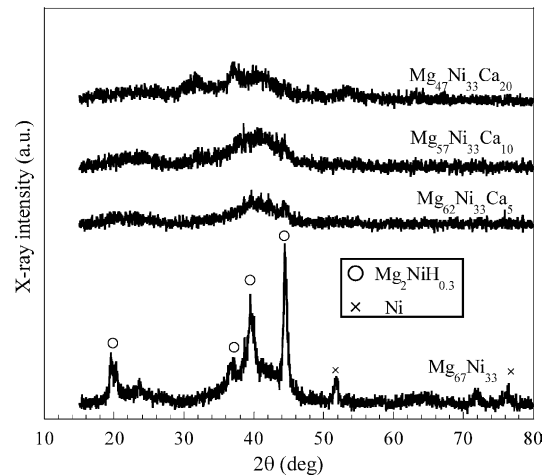


Fig. 2. X-ray diffraction patterns for the $Mg_{67-x}Ca_xNi_{33}$ mixtures after hydrogenation for 168 h at a temperature of 373 K and an initial hydrogen pressure of 5 MPa.

at an initial hydrogen pressure of 5 MPa are shown in Fig. 2. The binary $Mg_{67}Ni_{33}$ mixture forms the α -phase ($Mg_2NiH_{0.3}$ hydride), with minor expansions of the crystal lattice of the Mg_2Ni crystal, after hydrogenation, but all ternary mixtures (containing Ca) are induced to form an amorphous-like phase after hydrogenation. $Mg_{67-x}Ca_xNi_{33}$ amorphous alloys, produced by melt-spun, had reported to be an amorphous structure even after hydrogen absorption at 373 K [5].

The β -phase (Mg_2NiH_4), which is now well classified into three kinds of phases (LT1, LT2, and HT-phases) [6,7], forms after absorbing great amount of hydrogen. The LT-phases are low temperature phases and normally formed by hydriding the alloy below 510 K. The HT-phase, on the other hand, is high-temperature phase, and formed by hydriding at above 510 K. Fig. 3 shows XRD patterns for the $Mg_{67-x}Ca_xNi_{33}$

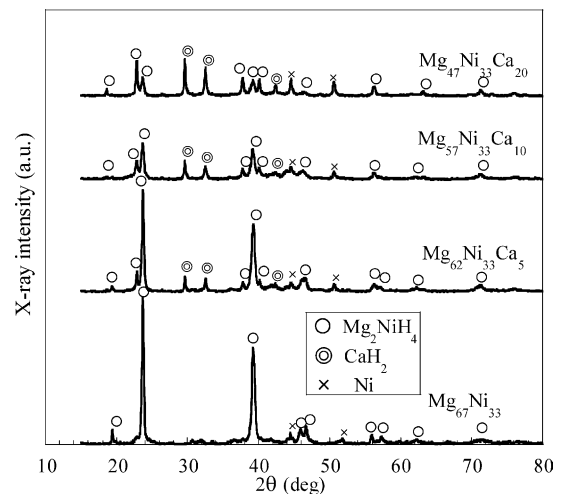


Fig. 3. X-ray diffraction patterns for the $Mg_{67-x}Ca_xNi_{33}$ mixtures after hydrogenation for 168 h at a temperature of 503 K and an initial hydrogen pressure of 3.5 MPa.

mixtures after hydrogenation for 168 h at a temperature of 503 K and at an initial hydrogen pressure of 3.5 MPa. The color of the binary powder changed orange after hydrogenation, that is a sign of formation of the LT2-phase [6,7], but the addition of Ca did not change the color of the ternary powders. Most of the X-ray diffraction peaks for the ternary powders after hydrogenation are very similar to that for the binary powder, indicating that the LT-phase (Mg_2NiH_4 hydride) also forms in the ternary mixtures. Furthermore, in the ternary mixtures, the CaH_2 hydride also forms, showing that a disproportionation reaction occurred in the ternary mixtures at 503 K. Total amount of the CaH_2 hydride in the ternary mixtures seem to increase with increasing Ca concentration in the mixtures, because of stronger X-ray intensities of the CaH_2 with higher Ca concentration.

DSC scans were performed at heating rate of 5 K/min for hydrogenated mixtures. Fig. 4 shows main temperatures for the maximum hydrogen desorption rate (hydrogen desorption temperatures) measured from the DSC curves. Note that the desorption temperatures for the ternary mixtures hydrogenated at 373 K are for amorphous-like phase, although that for the binary mixture is for the $\text{Mg}_2\text{NiH}_{0.3}$ hydride, and those for all mixtures hydrogenated at 503 K are for the Mg_2NiH_4 -type hydride (LT) phase. The CaH_2 hydride was not decomposed between heating ranges of the present DSC experiment. The hydrogen desorption temperatures for the binary alloy hydrogenated at 373 and 503 K are about 565 and 575 K, respectively, but those temperatures increase with increasing Ca concentration in the mixtures. The activation energy for hydrogen desorption (or hydride decomposition) can be estimated from the shift in the (endothermic) peak temperature for DSC measurements made at different heating rates [8], using

$$\ln\left(\frac{Q^2}{T}\right) = -\left(\frac{E}{RT}\right) + A \quad (1)$$

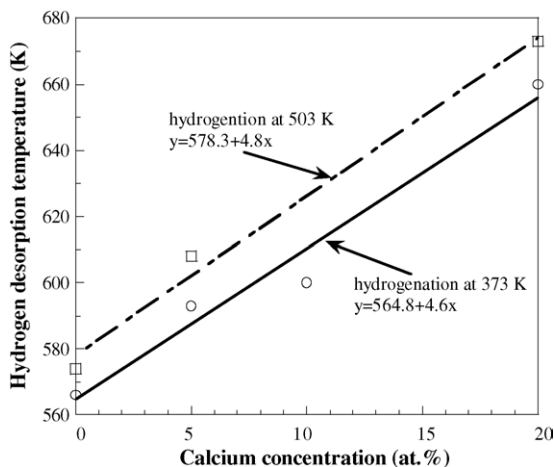


Fig. 4. Main hydrogen desorption temperatures measured from the DSC curves as a function of Ca concentration in the $\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ mixtures.

where, Q is the heating rate (K/min), T the peak temperature (K), R the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and E is the activation energy for hydrogen desorption (J mol^{-1}). The activation energies for hydrogen desorption for the binary, and ternary $\text{Mg}_{62}\text{Ni}_{33}\text{Ca}_5$ and $\text{Mg}_{47}\text{Ni}_{33}\text{Ca}_{20}$ mixtures after hydrogenation at 373 K was about 92, 91 and 168 J mol^{-1} , respectively, and those after hydrogenation at 503 K were about 92, 137 and 244 J mol^{-1} , respectively, indicating that substitution of Ca for Mg stabilizes the hydride phases. During heating the binary powder hydrogenated at 503 K in a DSC scan, small sharp endothermic peak (at about 500 K at heating rate of 5 K/min) was observed before the decomposition of the hydride (hydrogen desorption), probably due to the transformation of the LT-phase to the HT-phase. This small endothermic peak became small and shifted to low-temperature side with increasing Ca concentrations in the ternary powder.

4. Conclusions

$\text{Mg}_{67-x}\text{Ca}_x\text{Ni}_{33}$ elemental powder ($0 \leq x \leq 20$) mixtures were mechanically alloyed for up to 45 h, and effects of Ca substitution for Mg on phase variations after mechanical alloying and subsequent gas phase loading of hydrogen at temperatures of 373 and 503 K, and on their hydrogen desorption temperatures were investigated. The results obtained are summarized as follows:

1. MA led to the formation of the Mg_2Ni -type phase for all mixtures, although small amount of Ni remained in the mixtures, and the CaO oxide also formed in a Ca-rich mixture. The c/a ratio of the lattice parameters of the Mg_2Ni -type phase increased up to approximately 4% with increasing Ca concentration in the mixtures.
2. The binary mixture ($\text{Mg}_{67}\text{Ni}_{33}$) transformed to the α -phase ($\text{Mg}_2\text{NiH}_{0.3}$ hydride) and the LT-phase (Mg_2NiH_4 hydride) after hydrogenation at 373 and 503 K, respectively.
3. The ternary mixtures (containing Ca) were induced to form an amorphous-like phase after hydrogenation at 373 K, but they were disproportionated to the two kinds of hydrides, i.e., CaH_2 and Mg_2NiH_4 (LT-phase), after hydrogenation at 503 K.
4. The main hydrogen desorption (or hydride decomposition) temperature as well as activation energy for hydrogen desorption increased with increasing Ca concentration in the mixtures, indicating that substitution of Ca for Mg stabilizes the hydride phases.

References

- [1] R.B. Schwarz, MRS Bull. 24 (1999) 40–44.
- [2] G. Liang, R. Schultz, J. Alloys Compd. 356–357 (2003) 612–616.

- [3] J.H. Schneibel, D.S. Easton, J.A. Horton, B.S. Chao, L. Cantrell, Y. Li, R.C. Young, J. Ting, *J. Alloys Compd.* 350 (2003) 130–135.
- [4] K. Isogo, T. Shoji, H. Kimura, A. Inoue, *Mater. Trans., JIM* 41 (2000) 1486–1489.
- [5] S.I. Yamaura, H.Y. Kim, H. Kimura, A. Inoue, Y. Arata, *J. Alloys. Compd.* 339 (2002) 230–235.
- [6] H. Blomqvist, D. Noréus, *J. Appl. Phys.* 91 (2002) 5141–5148.
- [7] E. Rönnebro, J.O. Jensen, D. Noréus, N.J. Bjerrum, *J. Alloys Compd.* 293–295 (1999) 146–149.
- [8] H.E. Kissinger, *Anal. Chem.* 29 (1957) 1702–1706.