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Journal of Alloys and Compounds 293–295 (1999) 541–545

Journal of ALLOYS AND COMPOUNDS

Synthesis and hydriding/dehydriding properties of amorphous $Mg_2Ni_{1.9}M_{0.1}$ alloys mechanically alloyed from $Mg_2Ni_{0.9}M_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn) and Ni powder

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Abstract

Amorphous $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn) alloys were prepared by mechanical alloying of pseudo-binary $Mg_2Ni_{0.9}M_{0.1}$ intermetallic compounds and Ni powder. The crystal structures, thermal stabilities and hydriding/dehydriding properties of those alloys were characterized by powder X-ray diffraction, thermal analysis and conventional measurement of pressure composition isotherms. In spite of the difference in M element, all specimens formed amorphous structures by mechanical alloying. Owing to the substitution of Ca the amount of desorbed hydrogen increased from 1.8 mass% for M=none to 2.1 mass% for M=Ca by measurement of thermogravimetry. The dehydriding reactions occurred at temperatures below about 400 K in both alloys.

Keywords: Mechanical alloying; Mg–Ni Alloy; Hydrogen; Amorphous; Substitution

1. Introduction

Pure Mg metal absorbs hydrogen to form MgH_2 and the hydrogen content is as high as 7.6 mass% [1], which is one of the high values among hydrogen absorbing materials. In addition, it is rich in natural resources and the price is less expensive than the other metals consisting of hydrogen absorbing alloys. Therefore Mg based hydrogen absorbing alloys have a great potential for application such as hydrogen transportation and storage. However, in spite of the above favored features it is difficult for Mg based hydrogen absorbing alloys to apply for actual systems because high temperature such as above 550 K is required for reversible absorption and desorption of hydrogen.

The first publication on the Mg based hydrogen absorbing alloys has been presented by Reilly reporting the research on the Mg_2Cu [2]. Nevertheless Mg_2Cu does not react to hydrogen reversibly because of disproportionation. The same group reported that the intermetallic compound Mg_2Ni can be hydrogenated to form Mg_2NiH_4 rapidly without disproportionation [3]. The other Mg based hydrogen absorbing alloys such as Mg-rare earth systems [4], Mg–Al systems [5], Mg–Zn systems [6], and ternary or quaternary alloy systems have also been investigated to date. However, almost all the Mg based hydrogen absorbing alloys except Mg_2Ni disproportionated. Accordingly, improvement of the intermetallic compound Mg_2Ni attracts considerable attention. Moreover recently, it has been shown that a search [7,8] for new alloys with new compositions and structures differ from those of Mg and Mg_2Ni by means of mechanical alloying (MA).

It has been reported [9] that the synthesis of amorphous $Mg(Ni_{1-X}T_X)$ alloys by mechanical alloying of intermetallic compound Mg_2Ni and powder of Ni and T. Orimo et al., reported that amorphous MgNi formed $MgNiH_{1.9}$ whose hydrogen capacity is about 2.2 mass% [10]. However, in this method, homogeneity of synthesized substituted alloys seems to be insufficient. In addition, selection of T is limited because powder of some of elements suitable for hydrogen absorption are active in air and with moisture. In this work, therefore, we first prepared the pseudo-binary intermetallic compounds $Mg_2Ni_{0.9}M_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn, where none corresponds to $Mg_2Ni_{0.9}$) by conventional melt technique. And then the mixtures of $Mg_2Ni_{0.9}M_{0.1}$ and Ni powder were mechanically alloyed. Finally we established the

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PII: S0925-8388(99)00408-9

synthetic technique of the amorphous $Mg_2Ni_{1.9}M_{0.1}$ hydrogen absorbing alloys.

2. Experimental details

Pseudo-binary intermetallic compounds $Mg_2Ni_{0.9}M_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn) were prepared by using a vacuum high frequency induction furnace. These compounds were not annealed. The solidification structures, crystal structures and chemical compositions of those alloys were characterized by Scanning Electron Microscopy (SEM JMS Inc. JSM6400), Electron Probe Microanalyzer (EPMA Link Inc., QX2000), powder X-ray diffractometer (XRD Rigaku Inc., RINT2000 Cu–Ka) and chemical analysis (Seiko Inc., SPS4000), respectively. These ingots were crushed under Ar atmosphere into particles of less than 150 μm diameter. The mixtures of $Mg_2Ni_{0.9}M_{0.1}$ and Ni powder (~10 μm) the ratio of 1:1 were milled by using a planetary ball mill (Fritch Inc., Type P-5) for 25 h under 0.1 MPa of Ar atmosphere. The crystal structures, thermal stabilities, and hydriding/dehydriding properties of those milled alloys were characterized by powder X-ray diffraction, thermal analyses (Seiko Inc., SSC5200) and conventional measurement of pressure composition isotherms at 373 K. Thermal analysis (Differential Thermal Analysis; DTA, Thermogravimetry; TG, Differential Scanning Colorimetry; DSC) were carried out under purified Ar atmosphere under heating condition of 5 K/min. up to 773 K. The amounts of the samples were 0.03 g for TG and DTA and were 0.01 g for DSC.

3. Results and discussion

3.1. Solidification structures of $Mg_2Ni_{0.9}M_{0.1}$

The solidification structures of melted $Mg_2Ni_{0.9}M_{0.1}$ are classified into three types. Type 1 was observed for M=none, Ca and La. As the SEM image of M=Ca is shown in Fig. 1(a), the solidification structure of type 1 was almost single phase. As the result of EPMA measurements, composition of this phase was determined as $Mg_{1.98}Ca_{0.05}Ni$. Ca and La were substituted for Mg. Type 2 was found in the case of M=Y, Al and Si. The solidification structure of M=Si is shown in Fig. 1(b). There were three different phases where the major phase was Mg_2Ni and does not contain Si by EPMA data, the second phase was intermetallic compound Mg_2Ni_3Si, and the third phase was the eutectic phase of Mg and Mg_2Ni. Type 3 was observed in the case of M=Cu, Mn and Ni. The solidification structure of type 3 was almost single phase shown in Fig. 1(c) (M=Cu). However, there was a minor phase. Those EPMA data show that, the composition of the major phase was $Mg_{2.17}Ni_{1.00}Cu_{0.11}$, and the second phase was $Mg_{1.06}Ni_{2.00}Cu_{0.06}$. Consequently Cu and Mn was substituted for Ni. Fig. 2 shows powder X-ray diffraction profiles of melted $Mg_2Ni_{0.9}M_{0.1}$ (M=Ca, Si and Cu). These profiles give a good agreement with the above results of SEM observation and EPMA measurement.

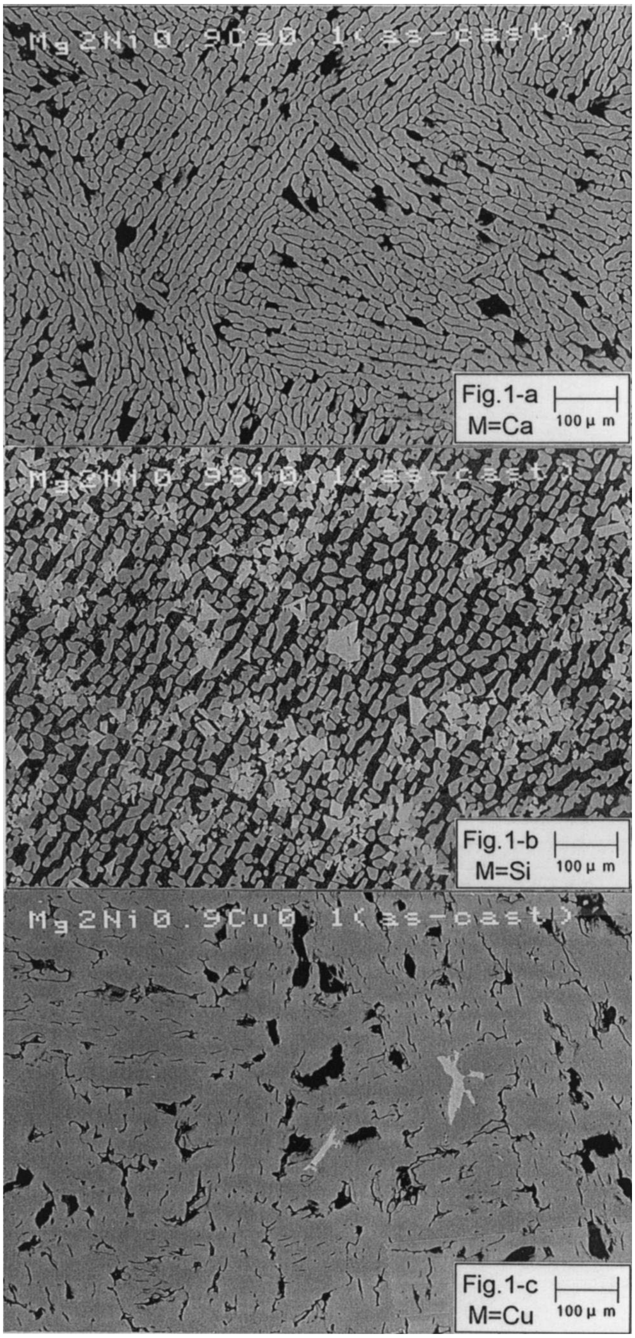

Fig. 1. SEM images of pseudo-binary $Mg_2Ni_{0.9}M_{0.1}$ (M=Ca, Si and Cu) intermetallic compounds melted by using a vacuum high frequency induction furnace.

3.2. Mechanical alloying

Fig. 3 shows the powder X-ray diffraction profiles of mechanically alloyed $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn, where none corresponds to $Mg_2Ni_{1.9}$). In spite of the difference in M element, all specimens formed amorphous structures by MA. However, in M=Y and Si specimens which solidification structures

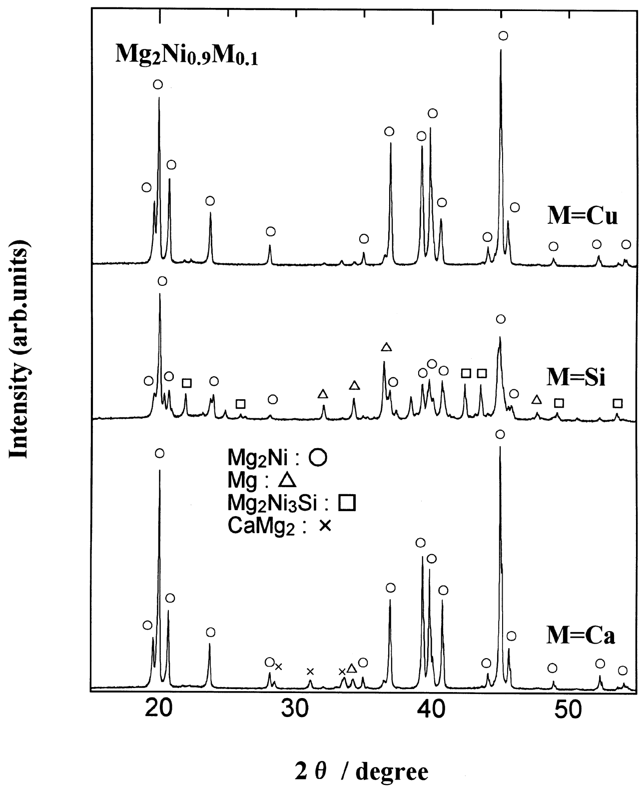

Fig. 2. X-ray diffraction profiles of melted $Mg_2Ni_{0.9}M_{0.1}$, where M=Ca, Si and Cu.

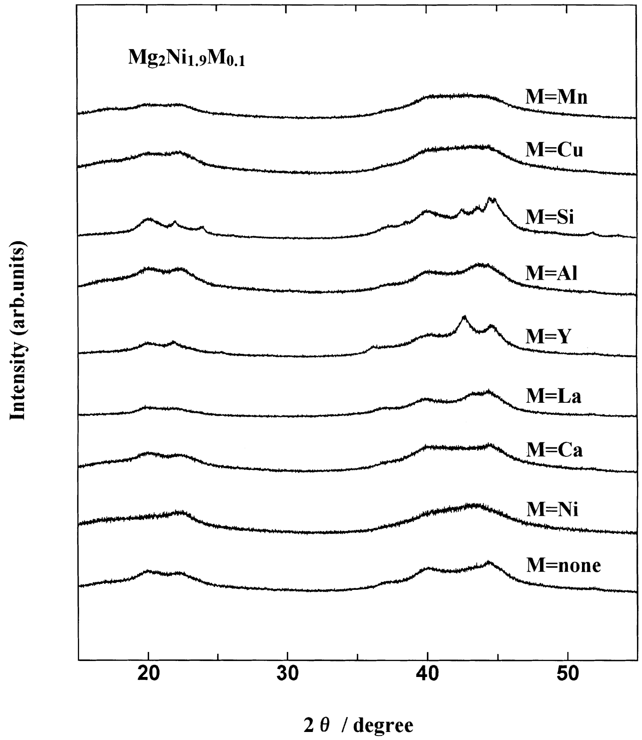

Fig. 3. X-ray diffraction profiles of mechanically alloyed $Mg_2Ni_{1.9}M_{0.1}$, where M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn.

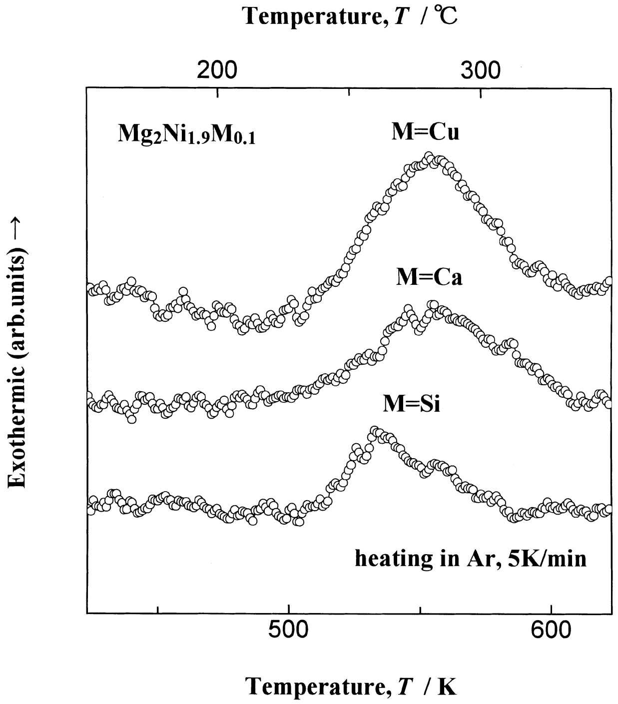

Fig. 4. Differential scanning calorimeter (DSC) profiles of mechanically alloyed $Mg_2Ni_{1.9}M_{0.1}$ (M=Cu, Si and Ca).

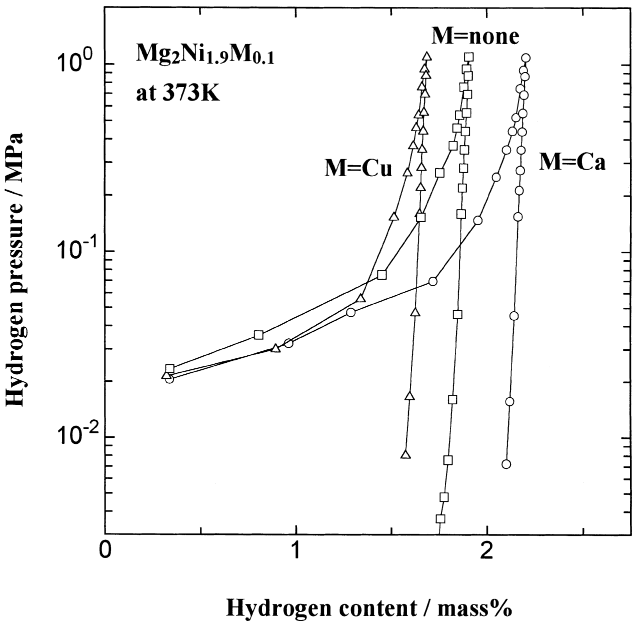

Fig. 5. Pressure composition isotherms of amorphous $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ca and Cu).

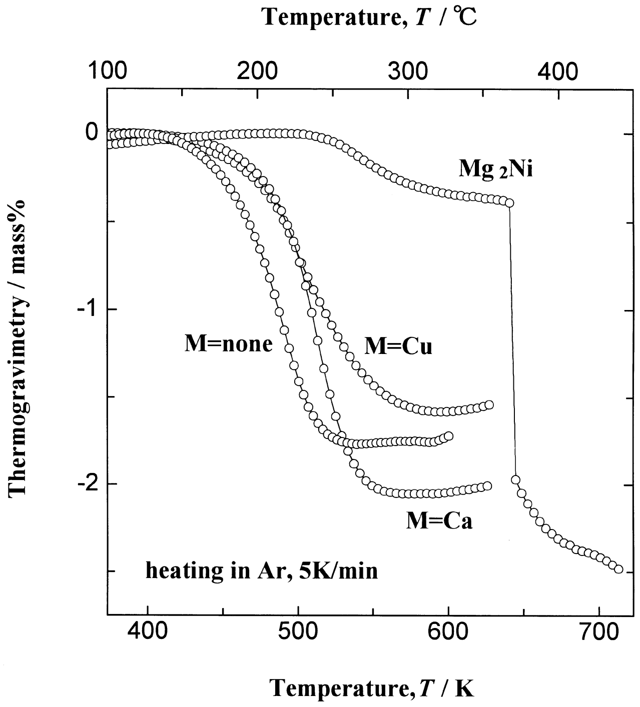

Fig. 6. Thermogravimetric (TG) profiles of hydrogenated amorphous $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ca and Cu) and crystalline Mg_2Ni.

consist of more than two phases, a few small broad X-ray diffract peaks were observed. Fig. 4 shows the DSC profiles of mechanically alloyed $Mg_2Ni_{1.9}M_{0.1}$ (M=Ca, Si and Cu). Exothermic peaks were observed from about 500 K. These peaks were due to crystallization of the amorphous phase because crystalline phases were observed in the samples after DSC measurement by X-ray diffraction. The similar exothermic peaks were also observed in other amorphous $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ni, Al and Mn). The peak area of these exothermic seems to be relevant to degrees of amorphous structure. In this study, we could not find out the clear difference of crystallization temperature depending on variety of M element. However, in all specimens, these crystallization reactions were observed at temperatures from around 500 K.

3.3. Hydriding/dehydriding properties

The pressure composition isotherms at 373 K of amorphous $Mg_2Ni_{1.9}$, $Mg_2Ni_{1.9}Ca_{0.1}$ and $Mg_2Ni_{1.9}Cu_{0.1}$ alloys are shown in Fig. 5. As we can see in these results, at 373 K hydrogen absorption occurred while hydrogen desorption hardly occur in those specimens. In the specimen of M=Ca, the total absorption hydrogen contents was 2.2 mass% while in the specimens of M=none and Cu, the total absorption hydrogen contents were 1.9, 1.7 mass%, respectively. Moreover, the clear equilibrium pressure of hydrogen absorption could not be observed in any specimens. Fig. 6 shows the TG profiles of hydrogenated amorphous $Mg_2Ni_{1.9}M_{0.1}$ (M=none, Ca and Cu). This figure also shows the TG profiles of the hydrogenated crystalline Mg_2Ni for comparison. It clearly shown that as the result of the structural modifications from crystal to amorphous, the starting temperatures of dehydriding reactions became lower. In the specimens of M=none, Ca and Cu, dehydriding reactions started at temperatures from around 400 K. Moreover, the amorphous hydrides desorbed hydrogen in the rang from 400 K to 550 K while crystalline hydride desorbed hydrogen suddenly at one given temperature. It is generally accepted that the distribution of potential energy for hydrogen site seems to be influenced by formation of an amorphous phase [11]. As the result of the structural modifications from crystal to amorphous, distribution of the potential energy for hydrogen site becomes broader. Hydrogen contents of all specimens are summarized in Table 1.

4. Conclusion

1. We established the synthetic technique of the amorphous $Mg_2Ni_{1.9}M_{0.1}$ hydrogen absorbing alloys containing homogeneous dispersion of various M element by means of mechanical alloying of melted $Mg_2Ni_{0.9}M_{0.1}$ and Ni powder.
2. Those amorphous alloys crystallized at temperatures from around 500 K.
3. As the result of the structural modifications from crystal

Table 1
The hydrogen contents of $Mg_2Ni_{1.9}M_{0.1}$

M element	None	Ni	Ca	La	Y	Al	Si	Cu	Mn
Absorption									
Hydrogen contents by PCT (mass%)	1.9	1.9	2.2	1.9	1.8	1.7	1.9	1.7	1.7
Desorption									
Hydrogen contents by TG (mass%)	1.8	1.7	2.1	1.5	1.7	1.6	1.8	1.6	1.6

to amorphous, the starting temperatures of dehydriding reactions lowered.

4. The desorption hydrogen contents increased from 1.8 mass% for M=none to 2.1 mass% for M=Ca by substitution. Moreover, dehydriding reactions were observed at temperatures from 400 K in both alloys.

Acknowledgements

This research has been conducted as one task of the WE-NET (World Energy Network [12]) projects supported by the government under consignment from New Energy and Industrial Technology Development Organization (NEDO).

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