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Synthesis of nano-structured b.c.c. Mg–Tm–V (Tm=Ni, Co, Cu) alloys and their hydrogen solubility

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Abstract

Mg–Tm–V (Tm=Ni, Co, Cu) alloys were synthesized by mechanical alloying. The structure characterizations by X-ray diffraction and electron diffraction revealed the prepared alloys to consist of nanocrystalline grains with b.c.c. structure, which was stable up to 573 K. It was found that synthesized $Mg_{1.0}Ni_{1.0}V_{1.0}$, $Mg_{1.0}Cu_{1.0}V_{1.0}$ and $Mg_{1.0}Co_{1.0}V_{1.0}$ alloys were able to absorb hydrogen up to 2.3, 1.44 and 0.95 wt.% at 3 MPa and 298 K, respectively. The plateau pressures of pressure–composition isotherms for these alloys were observed at 0.2–0.8 MPa and 298 K.

Keywords: Mg-based alloys; b.c.c.; Metal hydrides; Hydrogen; Mechanical alloying

1. Introduction

Recently, a lot of attention has been paid to b.c.c. solid solution alloys as promising candidates of hydrogen storage materials because of their high hydrogen storage capacities [1–4]. Ti–Cr(Mn)–V b.c.c. alloys have been reported to have a rather high solubility of hydrogen [3,5,6]. According to the mechanism of formation of the b.c.c. structure in the ternary alloy systems, the solubility of binary Laves phase, i.e. $TiCr_2$ or $TiMn_2$, in the b.c.c. V is crucial. In fact, the $TiCr_2$–V quasibinary phase diagram indicates that a large amount of $TiCr_2$ Laves phase dissolves in b.c.c. V at low temperatures [7].

Mg–Ni alloys have attracted growing interest as one of the most important hydrogen storage alloys because they are able to absorb a large amount of hydrogen and are relatively light in weight [8]. In the binary Mg–Ni alloy system, there are two intermetallic compounds, Mg_2Ni and $MgNi_2$. Mg_2Ni is an important hydrogen storage alloy forming on Mg_2NiH_4 hydriding with its hydrogen content higher than 3 wt.% [9–12]. On the other hand, the hydrogen solubility of the $MgNi_2$ phase has been reported to be negligibly small.

In this study, we studied the Laves structure of $MgTm_2$ (Tm=Ni, Co, Cu) intermetallic compounds and the possibility that $MgTm_2$ Laves phase would dissolve in b.c.c. V, as mentioned previously for the Ti–Cr–V ternary alloy system. However, in the case of the Mg–Tm–V system, alloying of these three elements is very difficult when the conventional melting–casting technique is used because of the large difference in melting temperatures of these elements. Moreover, the $MgTm_2$–V couple seems to be immiscible, as the enthalpy of mixing for the Mg–V couple is positive [13].

Recently, synthesis of metastable and amorphous phases by mechanical alloying has been extensively studied for binary mixtures with positive enthalpy of mixing [14–16]. For example, it has been reported that mechanical alloying of Fe–Cu powder mixtures yielded a nanocrystalline single-phase solid solution [14]. According to the equilibrium phase diagram of Fe–Cu, fcc Cu would not spontaneously dissolve in the b.c.c. Fe because of the positive enthalpy of mixing. In the case of mechanical alloying, enthalpy stored in the grain boundaries which derived from the energy created by heavy plastic deformation of powders and stress-field dislocations, could serve as the driving force for alloying.

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In this paper, the metastable b.c.c. structure for Mg–Tm–V (Tm=Ni, Co, Cu) immiscible systems was synthesized by mechanical alloying. The hydrogen absorption properties of the ternary b.c.c. phases were tested and discussed.

2. Experimental

In this study, magnesium (99.9%, <1 mm), nickel (99.9%, <200 μm), cobalt (99.0%, <200 μm), copper (99.9%, <200 μm) and vanadium (99.9%, <200 μm) powders were used. After pre-mixing the elemental powders to the desired average composition, the powder mixture was poured into a container together with 8-mm-diameter stainless balls and sealed under an argon atmosphere. The mechanical alloying was carried out for milling durations from 5 to 25 h at a speed of 12.3 rev/s by using a high-energy ball mill with a ball-to-powder weight ratio of 40:1.

The phase and microstructure of mechanically alloyed powders were characterized by X-ray diffraction (XRD) using Cu Kα radiation and transmission electron microscopy (TEM). The pressure–composition (P–C) isotherms were determined with a Sievert's apparatus at 298 K.

3. Results and discussion

Fig. 1 shows the XRD patterns for a $Mg_{1.0}Ni_{1.0}V_{1.0}$ powder mixture milled up to 25 h. In the early stages of milling, diffraction peaks from hcp Mg first disappeared and then the relative intensity of diffraction peaks from fcc Ni weakened with progression of milling. After milling for 25 h, XRD patterns were dominated by peaks from a typical b.c.c. structure, suggesting that elemental powders were well mechanically alloyed to the b.c.c. structure. Calculated lattice parameters of b.c.c. structure from XRD patterns are shown in Fig. 2. The lattice parameter increases at the beginning and then decreases with milling time. The increase in lattice parameter seems to correspond to the disappearance of diffraction peaks from Mg in the initial stage of milling, shown in Fig. 1. The atomic radius of Mg is larger than that of V. Therefore, if Mg with larger atomic size dissolves into b.c.c. V with a smaller atomic size, expansion of the b.c.c. lattice can be expected. Following expansion, the b.c.c. lattice shrinks with milling time because Ni has a smaller atomic size and starts to dissolve into b.c.c. V. From both Figs. 1 and 2 it can be concluded that the mechanical alloying of the $Mg_{1.0}Ni_{1.0}V_{1.0}$ powder mixture led to the formation of a ternary b.c.c. structure. Similar results were obtained for $Mg_{1.0}Co_{1.0}V_{1.0}$ and $Mg_{1.0}Cu_{1.0}V_{1.0}$ powder mixtures after milling for 25 h, as shown in Fig. 3.

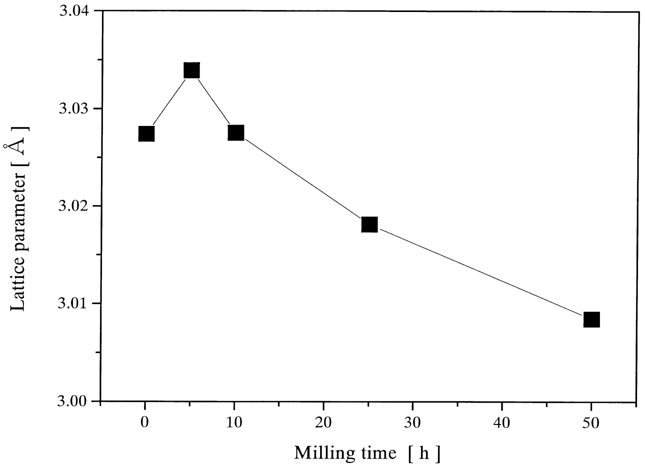

Fig. 2. Lattice parameter of b.c.c. crystals in $Mg_{1.0}Ni_{1.0}N_{1.0}$ after 25 h of milling.

For the above three different powder mixtures with different transition elements (Ni, Co and Cu), it should be noted again that Mg forms a binary Laves phase with

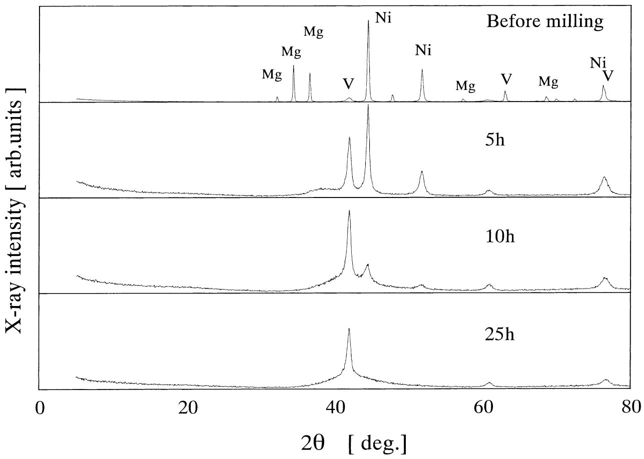

Fig. 1. X-Ray diffraction patterns for $Mg_{1.0}Ni_{1.0}V_{1.0}$ after different milling times.

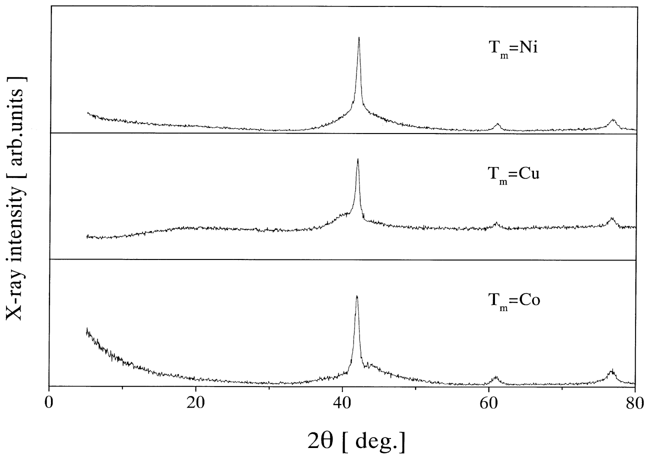

Fig. 3. X-Ray diffraction patterns for $Mg_{1.0}Tm_{1.0}V_{1.0}$ (Tm=Ni, Co, Cu) after 25 h of milling.

either of the above three transition elements. On the other hand, it is known that Laves structure in Mg–Fe and Mg–Mn binary alloy systems does not exist. In this study, milling of the powder mixtures of $Mg_{1.0}Fe_{1.0}V_{1.0}$ and $Mg_{1.0}Mn_{1.0}V_{1.0}$ was also tried. For these powder mixtures, even after extended milling the formation of ternary b.c.c. structures was not detected and only VFe and MnV phases were formed. The mechanism of the formation of the ternary b.c.c. phase for the MgTmV (Tm=Ni, Co, Cu) system is under study but it is believed that the existence of the Laves phase in the Mg–Tm (Tm=Ni, Co, Cu) binary alloy system might play an important role in the mechanism of alloy formation.

The above results, shown in Figs. 1 and 2, have been confirmed by TEM observations shown in Figs. 4. The selected-area diffraction (SAD) pattern (Fig. 4a) and the

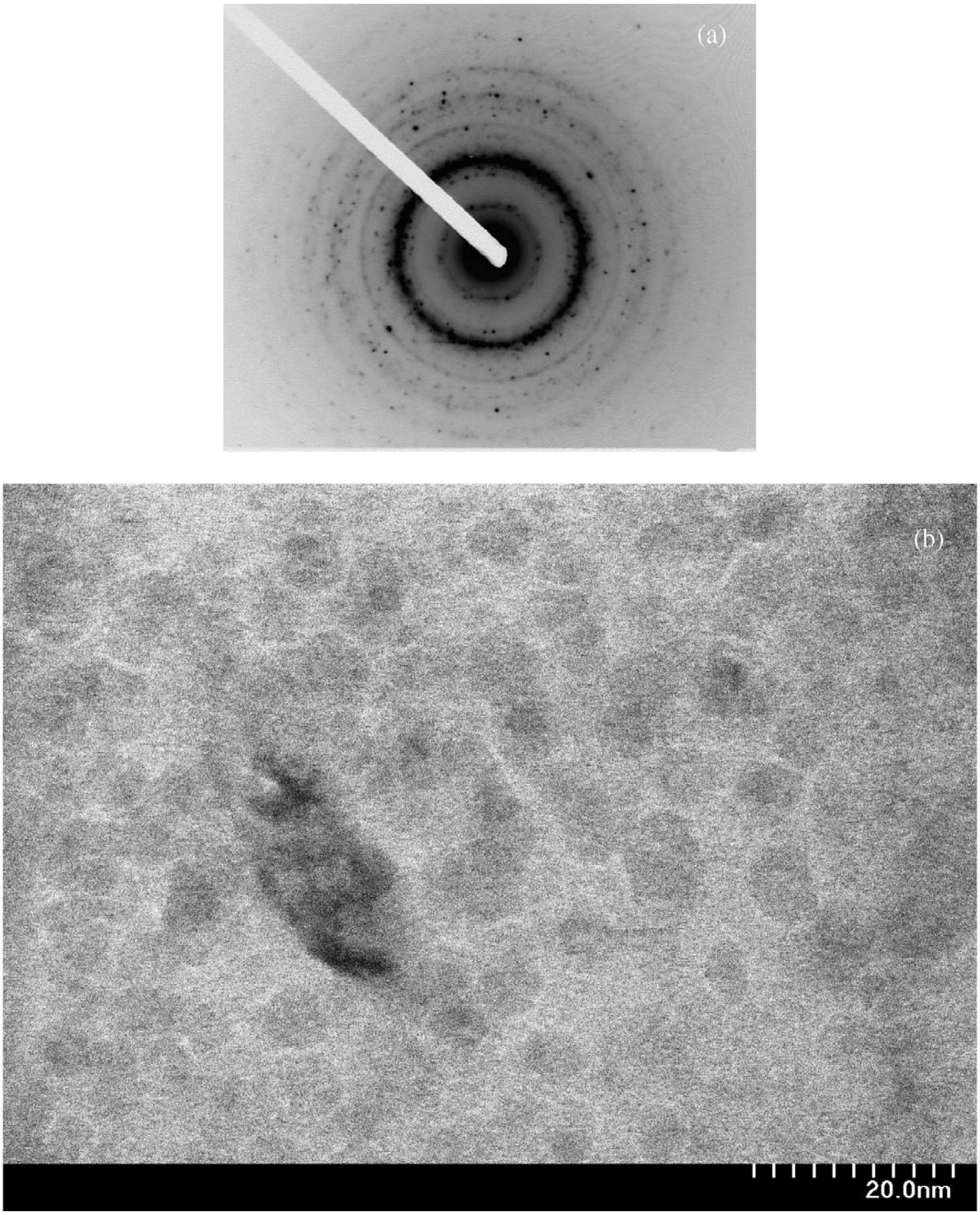

Fig. 4. SAD patterns (a) ZCM image; and (b) for $Mg_{1.0}Ni_{1.0}V_{1.0}$ after 25 h of milling.

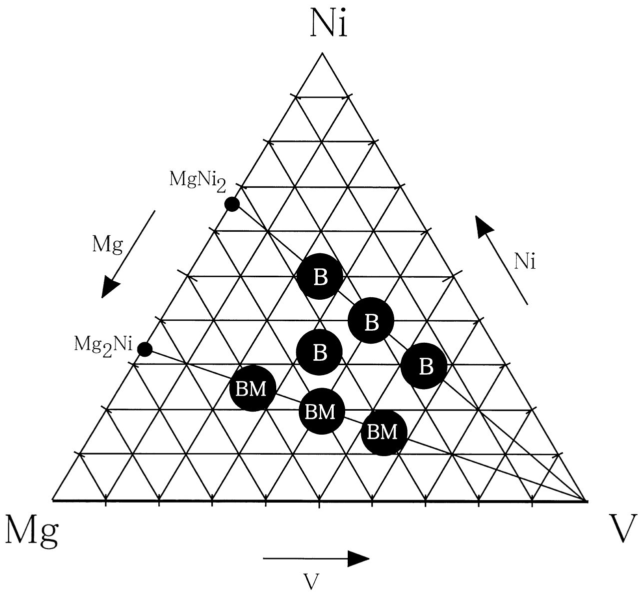

Fig. 5. Phase map according to composition for the MgNiV system; B, b.c.c.; BM, b.c.c.+Mg_2Ni.

corresponding Z-contrast mode (ZCM) image (Fig. 4b) show that the $Mg_{1.0}Ni_{1.0}V_{1.0}$ alloy synthesized by mechanical alloying for 25 h is composed of nano-sized b.c.c. grains, although some diffraction rings from Mg_2Ni with weak diffraction intensity are seen in the SAD pattern. The ZCM image clearly shows that the alloy consists of nano-sized grains <10 nm, with element concentrations somewhat fluctuated in the image.

In this study, Mg–Ni–V powder mixtures with a variety of compositions were investigated. Fig. 5 shows the synthesized phase map for the Mg–Ni–V system. It was found that the b.c.c. structure was formed for compositions on the line drawn from pure V to $MgNi_2$.

Fig. 6 shows PC isotherms of absorption for $Mg_{1.0}Tm_{1.0}V_{1.0}$ (Tm=Ni, Co, Cu) milled for 25 h at room temperature. A plateau corresponding to the hydride formation clearly appears on each isotherm. It should be noted that these alloys were not activated at higher temperatures and hydrogen pressures prior to measurement to prevent decomposition of the synthesized b.c.c. phase. In fact, the b.c.c. structure started decomposing at 623 K and the Mg_2Ni phase appeared. It was found that the synthesized $Mg_{1.0}Ni_{1.0}V_{1.0}$, $Mg_{1.0}Co_{1.0}V_{1.0}$ and $Mg_{1.0}Cu_{1.0}V_{1.0}$ alloys absorb hydrogen up to 2.4, 1.44 and 0.95 wt.% at 3 MPa and 298 K, respectively. These values are much higher than the calculated amount of hydrogen that can be absorbed by V and Mg in $Mg_{1.0}Tm_{1.0}V_{1.0}$ powder mixture at the corresponding temperatures if they were not alloyed. Even if V absorbs hydrogen and forms $VH_{2.0}$ hydride, the amount of hydrogen in the $Mg_{1.0}Ni_{1.0}V_{1.0}$ powder mixture should be only 1.4 wt.%, which is much lower than the value obtained from the isotherm shown in Fig. 6. It is well known that Mg hydride is extremely stable, the plateau pressure at room temperature should be far below our experimental pressure range. Moreover, if V is not alloyed, the formation of amorphous MgNi phase can be expected but it was found that MgNi amorphous alloy synthesized by mechanical alloying did not absorb hydrogen at room temperature.

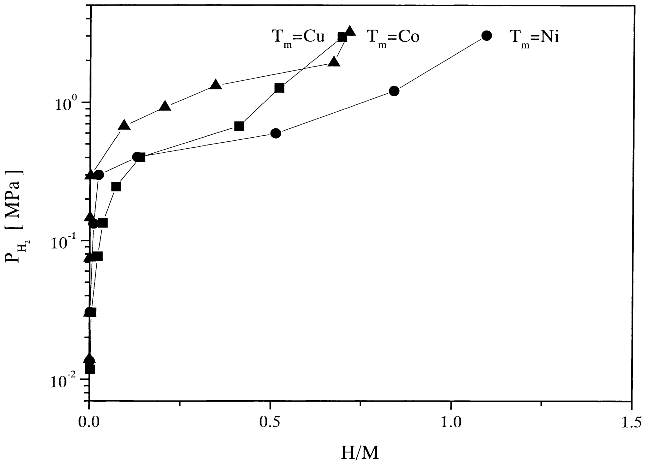

Fig. 6. PC isotherms for $Mg_{1.0}Tm_{1.0}V_{1.0}$ (Tm=Ni, Co, Cu) after 25 h of milling.

From the above discussions it can be concluded, consistently with the results obtained from XRD and TEM, that the ternary b.c.c. phase was synthesized by mechanical alloying of MgTmV (Tm=Ni, Co, Cu) powder mixtures.

4. Conclusions

In this study we have successfully synthesized ternary b.c.c. structures by mechanical alloying of $Mg_{1.0}Tm_{1.0}V_{1.0}$ (Tm=Ni, Co, Cu) powder mixtures. It was found that synthesized b.c.c. phases have a high hydrogen absorption capacity at 298 K and 3 MPa, i.e. 2.4 wt.% H for $Mg_{1.0}Ni_{1.0}V_{1.0}$, 1.14 wt.% H for $Mg_{1.0}Cu_{1.0}V_{1.0}$ and 0.95 wt.% H for $Mg_{1.0}Co_{1.0}V_{1.0}$. The existence of $MgTm_2$ (Tm=Ni, Co, Cu) plays an important role for the formation of ternary b.c.c. structure because the ternary b.c.c. phase was not formed for MgTmV (Tm=Fe, Mn) even after extended milling.

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