

Addition of Some Transition Elements and their Effects on the Electrochemical Properties of MgNi

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Abstract

In this study, some transition elements, Ag, Co, Pd, Re, Ru and Ti, at 6 and 10mol% compositions, were selected to ball mill with Mg₂Ni and Ni, and the effects of transition elements on the electrochemical properties of amorphous MgNi were investigated. Three distinct effects on the electrochemical properties of MgNi were found: Ti and Pd dissolved into the bulk of MgNi during ball milling and the degradation of discharge capacity was decreased by addition of Ti and Pd. Ag and Co also dissolved in the MgNi powder, but there was no appreciable influence on the electrochemical behavior of MgNi. Re and Ru neither dissolved into MgNi nor improved the properties of MgNi.

1. Introduction

Amorphous MgNi is attractive as an anode material of rechargeable Ni/MH batteries because of its high hydrogen storage capacity, low material cost, rich mineral resource, light weight and so on. However, practical application of MgNi is impeded by the rapid degradation of discharge capacity with charge/discharge cycle in alkaline solution, which was regarded as a result of the formation of Mg(OH)₂ during the charge/discharge¹⁻⁴. In our previous research, it was found that the formation of Mg(OH)₂ is not necessarily due to electrochemical reaction, but it is simply formed by chemical reactions with alkaline electrolyte^{2,3}.

Surface modification has been proved to be an effective method to improve the electrochemical properties of MgNi. Ball-milling of MgNi with graphite for a short time⁵⁻⁷ and vacuum deposition of carbon on MgNi⁸ increased the discharge capacity and the cycle life of MgNi. We also found that ball-milling aromatic compounds such as benzene (C₆H₆) and perylene (C₂₀H₁₂) with MgNi improved the discharge capacity and/or the cycle life of MgNi⁹. Other studies also reported that composition

modification (e.g., by alloying Ti^{6, 10-12}, V^{6, 11, 12}, Zr, Al¹¹, and Y¹³) with MgNi) resulted in a certain extent of improvement on the electrochemical properties of MgNi. These results suggest that the electrochemical properties, especially the cycle life of MgNi, could be improved if the formation of Mg(OH)₂ is suppressed by modification.

Alloying is one of the methods to improve physicochemical properties of hydrogen absorbing materials. As for amorphous MgNi, Orimo and Fujii¹⁴) had systemically studied hydriding properties of amorphous MgNi by Ni-site substitution with 3d-transition metals and Mg-site substitution by Zr, where the hydriding properties were examined on the basis of thermal analysis. However, no study on their electrochemical properties were carried out. In this study, some transition metal elements were selected as addition for MgNi modification, and the effects of these elements on the electrochemical properties of MgNi were investigated.

2. Experimental

In this study, Ag, Co, Pd, Re, Ru and Ti were used to modify MgNi. The purity and size of the metal powders are listed in the Table 1. Two compositions of addition were selected, 6mol% and 10mol%. The transition elements, Ag, Co, Pd, Ti, Re or Ru, were mixed with Ni and Mg₂Ni (the molar ratio of Ni and Mg₂Ni is 1:1) in prescribed weight fractions with the total weight of 2gram. Each mixture powder was ball milled for 80 hr under the same conditions as described previously^{9,15}). The discharge capacity of each kind of modified MgNi powders was also measured under the same conditions as before^{9,15}).

Table.1 Basic characteristic of the powders in this study.

	Ag	Co	Pd	Re	Ru	Ti	Ni	Mg ₂ Ni
Purity	99.9%			99.99%	99.9%	99.9%	99.8%	
Size	44μm	5μm	1μm	4-5μm		149μm	3-7μm	74μm

In order to examine the effects on prevention of Mg(OH)₂ formation, some testing powder was immersed into 6M KOH for 168 hr, and XRD patterns of these powders before and after the immersion were measured by Kα radiation of Cu by Phillips-PW1825 Automated Powder Diffractometer operated at 40 kV and 30 mA.

3. Results

The effects of 6mol% addition of transition elements on the discharge capacity are shown in Fig.1. For bare MgNi, the discharge capacity at the first cycle was 360mAh/g, and it decreased quickly with the increasing number of cycle to become less than 100mAh/g after about 10th cycles. Comparing with the bare MgNi, Pd and Ti modified MgNi showed almost the same discharge capacity at the first cycle. Their discharge capacities decreased with cycle number but the rates were slower than that of bare MgNi. For other elements, the discharge capacity at the first cycle did not increase, and decreased at almost the similar rate to that of the bare MgNi.

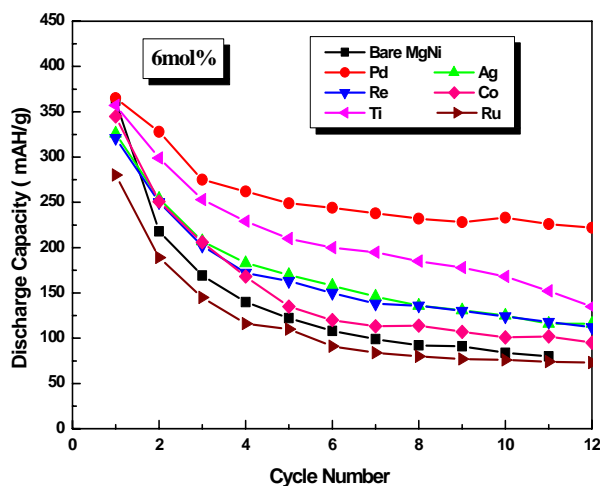


Fig . 1 Discharge capacity of modified MgNi by transition elements at 6 mol%.

Fig.2 shows the XRD patterns of the bare MgNi and modified MgNi by 6mol% addition. The bare MgNi showed the broad peak around

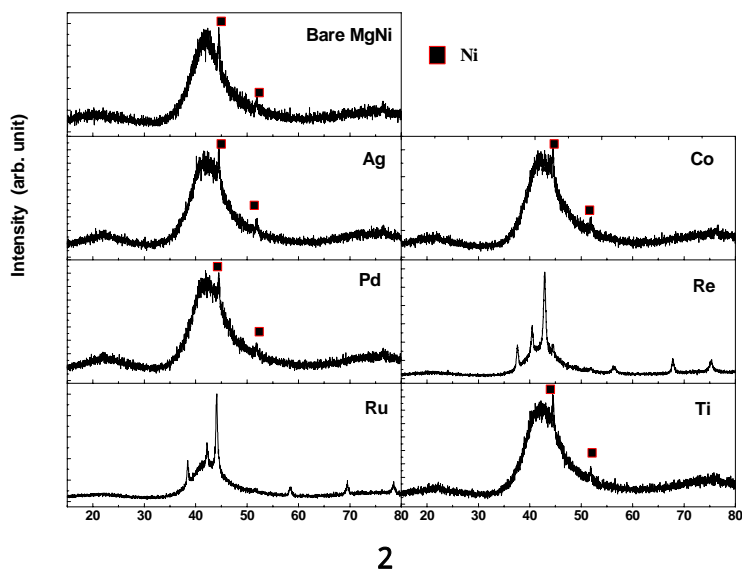


Fig. 2 XRD patterns of modified MgNi by 6 mol% transition elements.

41.5° assigned to amorphous structure and sharp peaks at 44.5° and 51.8° due to remaining crystalline Ni. After ball milling with Ag, Co, Ti and Pd, there was no observable peaks of these elements in the patterns of XRD, which indicates that these elements dissolved into the bulk of amorphous MgNi powder during ball milling.

However, for Re and Ru modification, the peaks of Re and Ru were very strong even after 80 hr ball milling and there appeared a broad peak at about 42° due to the formation of amorphous MgNi. These results suggest that amorphous MgNi was formed by ball milling Mg_2Ni and Ni, but at least a most part of Re and Ru did not dissolve into the bulk of MgNi; they were still in their crystalline states after ball milling.

In our previous studies^{2-4, 8, 9, 15)}, it has been concluded that, 1) the degradation of the discharge capacity of MgNi in alkaline solution was due to formation of $\text{Mg}(\text{OH})_2$, and 2) the cycle life of MgNi could be increased if the formation of $\text{Mg}(\text{OH})_2$ is suppressed. From this point, it is very important to understand whether these transition metals can prevent the formation of $\text{Mg}(\text{OH})_2$.

After the modified MgNi being immersed into 6M KOH for 168 hr, XRD patterns of testing powders were characterized as shown in Fig.3. For the bare MgNi, it is very clear that $\text{Mg}(\text{OH})_2$ peaks appeared after immersion, and the broad peak of amorphous structure became weaker than that for before immersion using the peak strength of Ni at 47° as a reference. This suggests that some of MgNi lost its amorphous structure because

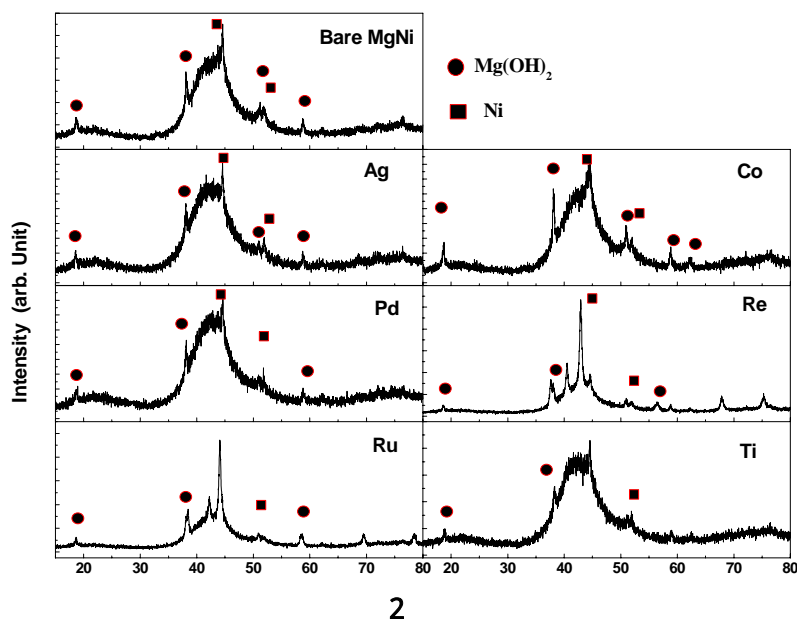


Fig. 3 XRD patterns of modified MgNi by 6 mol% transition elements after immersion in 6M KOH for 168 hr.

of the transformation of Mg into $\text{Mg}(\text{OH})_2$, resulting in disability of containing hydrogen atoms anymore.

For Ag and Co addition, the strength of the peaks of $\text{Mg}(\text{OH})_2$ were almost same as that in bare MgNi, indicating that the modification did not prevent the formation of $\text{Mg}(\text{OH})_2$. The loss of amorphous structure could also be observed. Together with the

results in Fig. 1, it is clear that 6mol% Ag and Co did not affect the corrosion receptivity of MgNi in alkaline solution.

With regard to Re and Ru addition, $Mg(OH)_2$ also was formed after immersion. In these cases, it was difficult to compare the strength of peaks of $Mg(OH)_2$ with that of bare MgNi, since the peaks of crystalline structure of Re and Ru were very strong. It should be mentioned, however, that the formation of $Mg(OH)_2$ was still in considerable extent. As for Ti and Pd, however, it was found that the formation of $Mg(OH)_2$ was not much appreciable as the bare one. These observations correspond to the slower decay rate of discharge capacity after Pd and Ti addition.

Fig.4 shows the effects of 10mol% addition on the discharge capacity, where one can see very similar features to those of 6mol% addition. For Pd and Ti, the discharge capacity of modified-MgNi was a little higher than that of bare one; the decay rate of discharge capacity with cycles was lower than that of bare MgNi, and even lower than that of 6mol% addition. These results indicate that 10mol% addition is more effective than 6mol% addition for Pd and Ti addition.

For Co addition, the discharge capacity for the first cycle was almost same as bare one, but the decrease of discharge capacity with cycles became slightly slower in comparison with bare MgNi. It was not so significantly improved, however, in comparison with the case of Pd and Ti addition. Ag addition also decreased the decay rates a little. Meanwhile, it seems that the effects of Ag and Co on the properties of MgNi had almost no clear dependence on the amount of Co and Ag addition.

As to Re and Ru addition, the discharge capacity for the first cycle was lower than that of bare MgNi, and the ability of hydrogen absorption also decreased with the cycles at the similar rates as bare MgNi. These observations mean that Re and Ru addition had almost no effect on the electrochemical properties of MgNi.

The XRD patterns of MgNi modified by 10mol% transition metals were also recorded before and after the immersion in 6M KOH for 168 hr. The results are showed in Fig. 5.

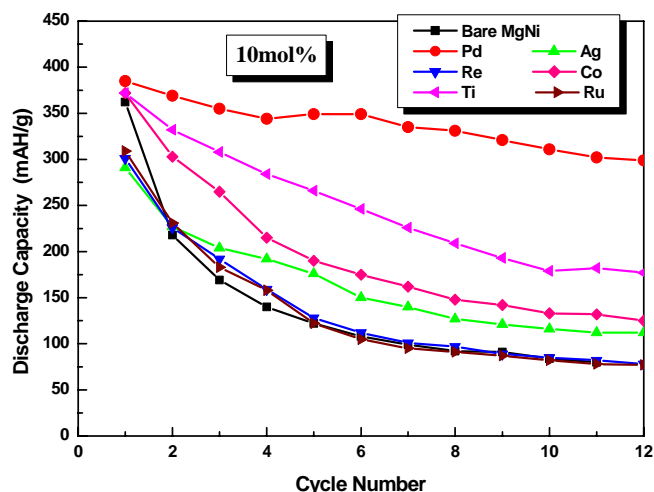


Fig . 4 Discharge capacity of modified MgNi by transition elements at 10 mol%.

In the case of Ag, there was no change in amorphous structure after 10mol% Ag addition, which is very similar to that of 6mol% Ag addition. There were also no significant peaks of Mg(OH)_2 after 168 hr immersion in 6M KOH, but the discharge capacity still decreased with the cycle number. As for Co, there was no observable difference between 10mol% Co-added MgNi and bare MgNi from XRD patterns. It means that Co can dissolve into the bulk of MgNi. However, stronger peaks of Mg(OH)_2 than that of MgNi could be seen after the immersion which might be responsible for the reduction in the discharge capacity with cycles.

For Ti and Pd (not listed in the figure), there was no difference between Ti (or Pd) added MgNi and bare MgNi from XRD, indicating that Ti (or Pd) dissolved into the bulk of MgNi powder during ball milling. In addition, there appeared no observable Mg(OH)_2 peaks after 168 hr immersion, suggesting that the 10mol% addition of Ti and Pd is very effective to prevent the formation of Mg(OH)_2 , as 6mol% Ti and 6mol% Pd.

Regarding Re and Ru, 10mol% addition gave very similar results as 6mol% addition. Namely, strong metallic peaks of Re or Ru could be found after ball milling with Mg_2Ni and Ni, and Mg(OH)_2 was also formed during the immersion in KOH solution. These results indicate that Re or Ru addition in MgNi has no effects on the electrochemical properties of MgNi except for the lower discharge capacity at the first cycle.

4. Discussion

As mentioned above, the effects of compositional modification of the amorphous MgNi on the electrochemical properties could be classified into three distinct kinds. These effects are discussed in the present section.

1) Modification by Pd and Ti:

The discharge capacity of modified MgNi did not change much at the first cycle, but the degradation of discharge capacity was significantly suppressed by Ti or Pd addition. In this respect, Pd was more effective than Ti. The effectiveness of addition was greater for 10mol% than 6mol% addition for both Ti and Pd. These electrochemical properties corresponded well with the properties that the addition of Ti and Pd into MgNi could prevent the formation of Mg(OH)_2 .

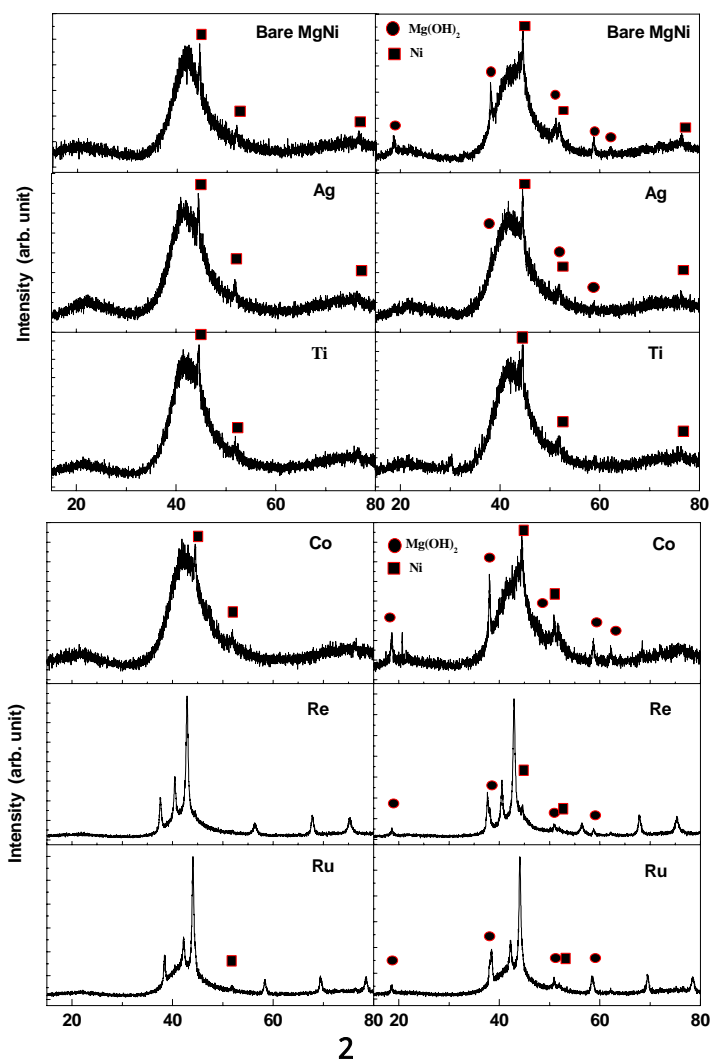


Fig. 5 XRD patterns of modified MgNi by 10 mol% transition elements before (left) and after (right) immersion in 6M KOH for 168 hr.

Han *et al.*¹⁰⁾ also observed that substitution of Ti for Mg in amorphous MgNi could increase the lifetime of MgNi in alkaline solution because the formation of titanium oxide layer on the surface of powder prevents the further oxidation of Mg. In the present study, Ti replaced both Mg and Ni in MgNi bulk. It was also found that Ti could prevent the oxidation of Mg. We also found that substitution of Ni by Ti (10mol%) resulted in not only the increase in lifetime of MgNi but also the significant increase in the discharge capacity (540mAh/g at first cycle, almost 1.5 times of that of bare MgNi for first cycle). These results indicate that the properties of MgNi after Ti modification are closely related with the composition and substitution site of Ti atoms in MgNi. More experimental work, however, is required in this aspect.

For the Mg-Ni alloy system, effects of Pd on Mg₂Ni were studied by Zaluski *et al.*¹⁶⁾ and Kohno *et al.*¹⁷⁾, and they believed that the improved hydrogen absorption ability by Pd addition is attributable to the catalyst effect of Pd. However, as for amorphous MgNi, our research¹⁵⁾ proved that the improvement by Pd-modification was due to the suppression of Mg(OH)₂ formation in alkaline media. The XRD results after long time immersion in this paper confirmed our explanation.

2) Modification by Ag and Co:

These two elements, Ag and Co, could dissolve into the bulk of MgNi during ball milling with Mg₂Ni and Ni at both 6 and 10mol% concentrations. There was, however, no significant effect on the electrochemical properties of MgNi; only some slower degradation in the discharge capacity was observed. According to Orimo and Fujii¹⁴⁾, Co addition gave neither the change in the structure of MgNi nor the hydriding properties. These observations were very similar to the results of the present study.

3) Modification by Re and Ru:

For Re and Ru, ball milling Re and Ru with Mg₂Ni and Ni did not make Re and Ru dissolve into the MgNi powder. Most parts of Re and Ru were still in metallic state even after 80 hr ball milling for both 6 and 10mol%. No significant effect on the electrochemical properties of MgNi was observed, except for the lower discharge capacity at the first cycle in comparison with the bare MgNi.

Table. 2 Lattice type and radius of some transition elements.

	Mg	Ni	Ag	Co	Pd	Ti	Re	Ru
Structure	A3	A1	A1	A3	A1	A3	A3	A3
Radius(Å)	1.60	1.25	1.45	1.25	1.38	1.45	1.37	1.33

The lattice structure and radius of transition elements used in this study are listed in the Table 2. It can be seen that for all of the transition elements studied the radiuses are between those of Mg and Ni. But there appears any clear relation between the radius of added-atom and/or the lattice structure and the properties of modified powders. In our previous research¹⁵⁾, it was found that after surface modification of MgNi by Pd prepared by ball milling, 6 and 10mol% Pd dissolved into the lattice of MgNi uniformly after 2 hr ball milling, and this transformation was very important for the improvement of the cycle life of MgNi in alkaline solution. However, as for Re, it's atomic radius is 1.37Å, which is almost the same as that of Pd. But Re did not dissolve into MgNi and was still in crystal state even after ball milling with Mg₂Ni and Ni for 80 hr. Addition of

Re had no effects on the electrochemical properties of MgNi. The roles of Ru are very similar with that of Re. Meanwhile, it was found ¹⁴⁾ that Co and Ti can dissolve into the amorphous structure of MgNi. These results suggest that the relationship between the lattice structure and/or radius of the transition elements with their effects on the MgNi electrode properties is still open to question.

5. Summery

In this study, some transition elements at 6 and 10mol% compositions were selected to ball mill with Mg₂Ni and Ni to modify amorphous MgNi, and three distinct effects on the electrochemical properties of MgNi were observed: 1) the degradation of discharge capacity was greatly suppressed by Ti and Pd addition after Ti and Pd dissolved into the bulk of MgNi, 2) Ag and Co also dissolved in the MgNi powder, but there was no considerable influence on the electrochemical properties of MgNi, 3) Re and Ru neither dissolved in the MgNi nor improved the properties of MgNi.

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REFERENCES

1. W. Liu, Y. Lei, D. Sun, J. Wu and Q. Wang: *J. Power Sources* **58** (1996) 243-247.
2. Y. Hatano, T. Tachikawa, D. Mu, T. Abe, K. Watanabe and S. Morozumi: *J. Alloys and Compounds* **330-332** (2002) 816-820.
3. D. Mu, Y. Hatano, T. Abe and K. Watanabe: *J. Alloys and Compounds* **334** (2002) 232-237.
4. T. Abe, T. Tachikawa, Y. Hatano and K. Watanabe: *J. of Alloys and Compounds* **330-332** (2002) 792-795.
5. C. Iwakura, S. Nahara, H. Inoue and Y. Fukumoto: *Chem. Commun.* (1996) 1831-1832.

6. C. Iwakura, H. Inoue, S. Nohara, R. Shin-ya, S. Kurosaka and K. Miyanohara: J. Alloys and Compounds **330-332** (2202) 636-639.
7. C. Iwakura, H. Inoue, S. G. Zhang and S. Nohara: J. Alloys and Compounds **293-295** (1999) 653-657.
8. T. Abe, S. Inoue, D. Mu, Y. Hatano and K. Watanabe: J. of Alloys and Compounds, **349** (2003) 279-283.
9. T. Ma, Y. Hatano, T. Abe and K. Watanabe: Material Transactions **43** (2002) 2711-2716.
10. S. C. Han, P. S. Lee, J. Y. Lee, A. Züttel and L. Schlapbach: J. Alloys and Compounds **306** (2000) 219-226.
11. S. C. Han, J. J. Jiang, J. G. Park, K. J. Jang, E. Y. Chin, and J. Y. Lee: J. Alloys and Compounds **285** (1999) L8-L11.
12. C. Iwakura, S. Nohara and H. Inoue: Solid State Inoics **148** (2002)499-502.
13. S. Nohara, K. Hamasaki, S. G. Zhang, H. Inoue and C. Iwakura: J. Alloys and Compounds **280** (1998) 104-106.
14. S. Orimo and H. Fujii: Appl Phys. **A72** (2001) 167-186
15. T. Ma, Y. Hatano, T. Abe and K. Watanabe: J. of Alloys and Compounds, in press.
16. L. Zaluski, A. Zalska, and J. O. Strom-Olsen: J. Alloys and Compounds **217** (1995) 245-249.
17. T. Kohno, M. Yamamoto and M. Kanda: J. Alloys and Compounds **293-295** (1999) 643-647.