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Synthesis of Nonstoichiometric Amorphous Mg-Based Alloy Electrodes by Mechanical Milling

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Nonstoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were synthesized by mechanical milling the crystalline Mg₂Ni alloy with Ni and/or V powders. All the nonstoichiometric amorphous Mg-based alloys result in Mg-based alloy electrodes with very high discharge capacities by comparison with crystalline Mg₂Ni alloys. The results indicate that nonstoichiometric amorphous Mg-based alloys can be obtained either by increasing the Ni content, adding a range of other elements, or both, using a mechanical milling method. The nonstoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a method of achieving better Mg-based alloy electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of vanadium additions.

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Mg-based hydrogen storage alloys are promising energy conversion and storage materials because they possess very high hydrogen storage capacities and magnesium is abundant in nature, light in weight, and relatively low in cost. For a long period, it has been thought that Mg-based hydrogen storage alloys, unlike AB₅-type hydrogen storage alloys, were unsuitable for Ni-MH negative electrodes because of their slow hydriding/dehydriding kinetics at ambient temperature and their susceptibility to corrosion in alkaline solution. In recent years, it has been shown that the most effective way for Mg-based hydrogen storage alloy electrodes to achieve high discharge capacities is by mechanical alloying (MA)¹⁻⁴: $\text{Mg} + \text{Ni} \rightarrow \text{MgNi}$ and mechanical milling (MM) the Mg-based hydrogen storage alloys with Ni powders.⁵⁻¹²

After mechanical milling, the most important change in the high discharge capacity Mg-based alloys is that they have completely or mainly amorphous structures. This has been demonstrated by X-ray diffraction (XRD) analysis,^{1,2-11} electron diffraction, and transmission electron microscopy (TEM).^{4,5,7,8,10} After ballmilling the Mg-based hydrogen storage alloys with Ni powders,⁵⁻⁸ the composition has the formula MgNi because the reaction during the ballmilling process may be expressed by the equation: $\text{Mg}_2\text{Ni} + \text{Ni} \rightarrow 2\text{MgNi}$. There are many possibilities; for example, the Mg could be replaced by Al,^{6,9} Ti,¹¹ Zr,¹¹ or V⁴ and Ni could be substituted by one or more elements, such as Co, Mn, Si, Cu, Ti, Zn, Fe, Zr, and so on.^{1-3,9} All the results so far have proved that the amorphous structure of Mg-based alloys is a key factor in achieving a large discharge capacity.¹⁻¹¹ MM nanocrystalline Mg₂Ni alloy¹² has only 175 mAh/g at a small discharge current density of 10 mA/g which is a low result compared with amorphous Mg-based alloys in this paper (about 400 mAh/g, at a discharge current density of 50 mA/g) and other papers.¹⁻⁹

For the crystalline hydrogen storage alloys, it is well known that their stoichiometry is the most important factor to achieving high storage capacity. That is why the hydrogen storage alloys usually are classified into four types: AB₅ (e.g., LaNi₅), AB₂ (e.g., ZrMn₂), AB (e.g., TiFe), and A₂B (e.g., Mg₂Ni). The alloy components A and B can be substituted by many other elements.

In this work, nonstoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were synthesized by mechanical milling the crystalline Mg₂Ni alloy with Ni and/or V powders. All the nonstoichiometric Mg-based alloys having amorphous structures, result in Mg-based alloy electrodes with very high discharge capacities by comparison with crystalline Mg₂Ni alloys.

Table I. The compositions of ballmilled alloys.

Mg ₂ Ni, Ni, and V ratio (molar)	Alloy formula	Name
Mg ₂ Ni + Ni	MgNi (Mg _{0.5} Ni _{0.5})	A
Mg ₂ Ni + 1.28 Ni	MgNi _{1.14} (Mg _{0.467} Ni _{0.533})	B
Mg ₂ Ni + Ni + 0.1 V	MgNiV _{0.1} (Mg _{0.476} Ni _{0.476} V _{0.048})	C
Mg ₂ Ni + Ni + 0.2 V	MgNiV _{0.2} (Mg _{0.455} Ni _{0.455} V _{0.09})	D
Mg ₂ Ni + Ni + 0.4 V	MgNiV _{0.4} (Mg _{0.417} Ni _{0.417} V _{0.166})	E
Mg ₂ Ni + 1.28 Ni + 0.1 V	MgNi _{1.14} V _{0.1} (Mg _{0.446} Ni _{0.509} V _{0.045})	F

Experimental

Alloy preparation and characterization.—The metal Ni (100 mesh, 99.7%) and V (-325 mesh, 99.5%) powders were obtained from the Aldrich Chemical Company. The induction melted (IM) Mg₂Ni alloy was supplied by Santoku Metal Industry Co., Japan.

Mechanical milling was performed with a Fritsch (P5) planetary ball mill. The vial and balls were made from stainless steel and hardened steel, respectively. To obtain more active alloy powders, the Mg₂Ni alloy was mixed and ballmilled with Ni and V powders for a period of about 70 h at 200 rpm in an argon atmosphere. The alloy compositions are listed in Table I. After milling, the powders were examined by XRD. XRD analysis was conducted using a Philips PW1010 X-ray diffractometer with Cu K α radiation. Morphologies and X-ray mapping analyses of the powdered alloys were conducted using a Leica Stereoscan 440 scanning electron microscope (SEM) and Oxford ISIS system using an OXFORD Link Pentatet detector.

Fabrication of electrodes and electrochemical measurements.—The IM Mg₂Ni alloy was crushed into powder and mixed with Ni powder in the weight ratio of 1:1 to make electrodes. The hydrogen storage alloy powders obtained from MM were also mixed with Ni powder in the weight ratio of 1:1 for electrode preparation. The hydride electrodes were fabricated by mixing the resultant powders with polyvinyl alcohol (PVA) solution and pasting them into a foamed nickel matrix, which acted as the current collector for the electrode. After being compressed, the hydride electrodes were immersed as negative electrodes in a 6 M KOH solution together with a NiOOH/Ni(OH)₂ counter electrode. A mercury oxide electrode (Hg/HgO) was used as the reference electrode. The electrochemical charge-discharge properties of the alloys were measured using a battery test unit controlled by a computer at 25°C. In the charge-discharge cycle tests, the charge cycle was commenced using

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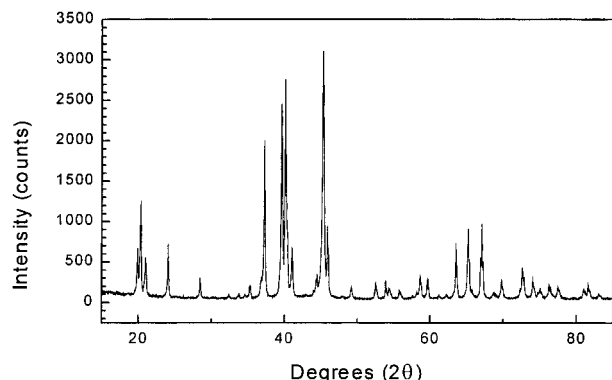


Figure 1. XRD pattern of the induction melting Mg_2Ni alloy.

a current density of 100 mA per gram of hydrogen storage alloy for 10 h. Then, after a 1 min rest, the discharge was continued using a current density of 50 mA/g until the voltage of the negative electrode against the mercury oxide electrode reached -0.6 V. The discharge capacities were calculated based on the total weight of the alloys.

Results and Discussion

Mg-Ni alloys.—The XRD pattern of the IM Mg_2Ni is shown in Fig. 1, which indicates a single Mg_2Ni phase. Figure 2 shows the XRD patterns of the IM Mg_2Ni alloy ballmilled with Ni powders in different ratios, indicating that homogenous amorphous MgNi and $\text{MgNi}_{1.14}$ were formed: $\text{Mg}_2\text{Ni} + 1.28 \text{ Ni} \rightarrow 2\text{MgNi}_{1.14}$. Orimo *et al.*¹³ reported that the high resolution TEM image and its diffraction pattern of compound Mg_2Ni ballmilled with Ni powder (molar ratio: 1:1, *e.g.*, Mg-50 atom % Ni, or MgNi) shows that an amorphous structure was obtained. The ballmilled alloys of the composition of Mg-33 atom % Ni, Mg-38 atom % Ni, and Mg-43 atom % Ni only have a nanostructure or a mixture of partial nanostructure and partial amorphous structure.¹³ This means that decreasing the Mg content may cause more difficulty in obtaining an amorphous structure for Mg-Ni alloys. Our result indicates that an amorphous structure can be obtained even if the nickel content is increased.

The hydrogen storage alloy Mg_2Ni reacts with H_2 readily at 325°C and 300 Pa, and the reaction in the plateau region can be expressed by the equation: $\text{Mg}_2\text{Ni} + \text{H}_2 \leftrightarrow \text{Mg}_2\text{NiH}_4$.¹⁴ The theoretical electrochemical capacity of hydride Mg_2NiH_4 is 999 mAh/g. However, the maximum hydrogen content of the amorphous MgNi region, 2.2 wt %, corresponds to a formula of $\text{MgNiH}_{1.9}$,¹³ and a calculated electrochemical capacity of 613 mAh/g.

The decrease in the discharge capacities of the crystalline IM Mg_2Ni alloy and the amorphous MgNi and $\text{MgNi}_{1.14}$ alloys after repeated charge-discharge cycles at a discharge current density of 50 mA/g is shown in Fig. 3. The discharge capacities of the alloys were calculated using their total weights. The crystalline IM Mg_2Ni alloy has a very low discharge capacity of only about 20 mAh/g (because of its poor hydriding kinetics at 25°C) while alloys A and B have much higher capacities. The initial discharge capacities of amorphous alloys A and B are approximately the same: 336 mAh/g, much higher than that of crystalline IM Mg_2Ni compound. After several charge-discharge cycles, the discharge capacities of both alloys A and B decrease rapidly. But nonstoichiometric amorphous alloy B has a slightly better cycle life than that of alloy A. This result encourages us to add other elements in a different way from traditional substitution, making nonstoichiometric Mg-based alloy electrodes.

Nonstoichiometric Mg-Ni-V alloys.—It has been well known since the 1960s that amorphous metals and alloys can be made by rapid quenching from the vapor or the liquid phase. A large number of investigations have shown that amorphous metals and alloys have the features of new alloy compositions and new atomic configurations which are totally different from those of crystalline alloys.

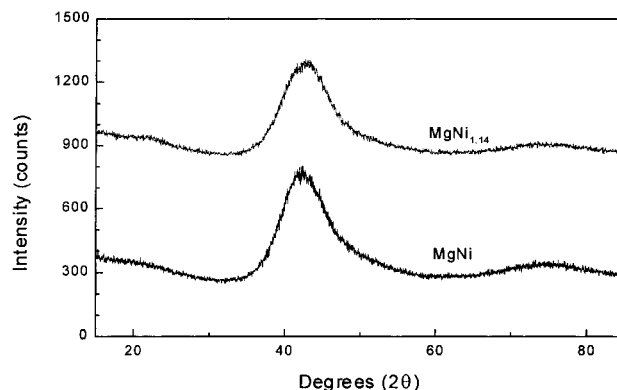


Figure 2. XRD patterns of IM Mg_2Ni alloy ballmilled with Ni powders in different ratio.

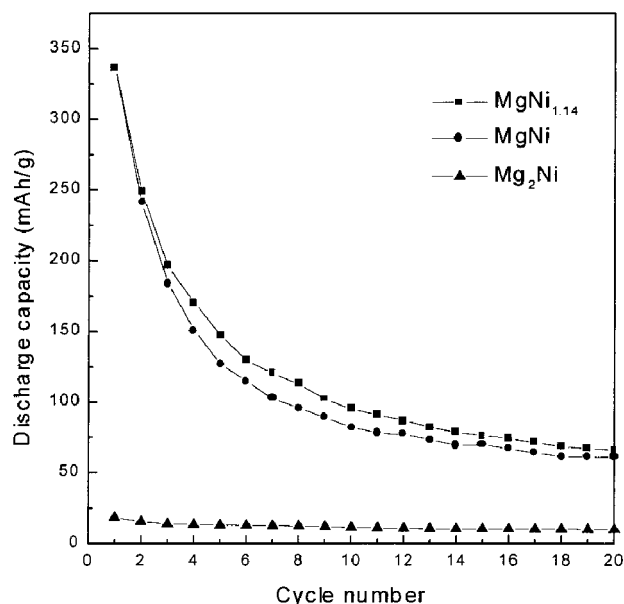


Figure 3. Decrease in the discharge capacities of the crystalline IM Mg_2Ni alloy and the amorphous MgNi and $\text{MgNi}_{1.14}$ alloys after repeated charge-discharge cycles at a discharge current density of 50 mA/g.

These features enable various kinds of characteristics to be achieved, such as excellent mechanical properties, useful physical properties, and unique chemical properties¹⁶⁻²¹ which have not been obtained for conventional crystalline alloys. Recently, solid-state amorphization by MA and MM have become the most effective methods for obtaining amorphous alloys.²²⁻³² The amorphous composition range achievable by MA is normally larger than that of other techniques. Lee and Koch³³ have reported that the MA Ni-Nb alloy system has a wider amorphous composition range than that of melt quenching. Therefore, it seems likely that it would be possible to synthesize nonstoichiometric amorphous MgNi alloy by adding other elements to MgNi alloy using the MA or MM method.

The XRD patterns of nonstoichiometric alloys C, D, E, and F are shown in Fig. 4. The patterns indicate that alloys C, D, E, and F are amorphous alloys. This conclusion was also confirmed by the results of differential thermal analysis (DTA) and TEM electron diffraction. These solid reactions correspond to the following reaction



where x and y are molar fractions of Ni and V, respectively. Thus,

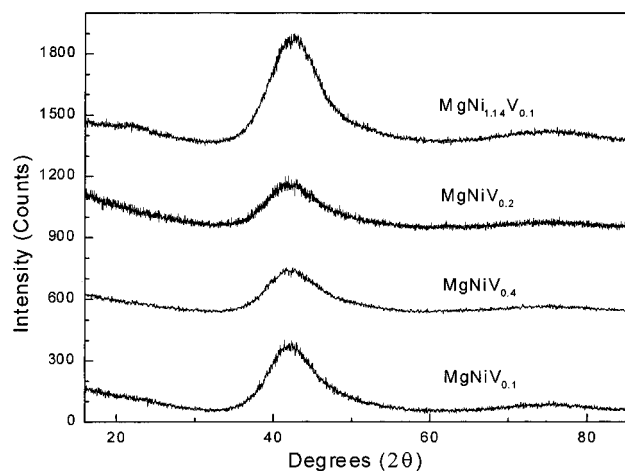


Figure 4. XRD patterns of nonstoichiometric alloys C, D, E, and F.

different amounts of vanadium can be added to the amorphous Mg-Ni alloy to make a range of nonstoichiometric Mg-based alloys without changing their basic amorphous structure.

Figure 5a shows the SEM micrograph of the alloy C powders while Fig. 5b is the micrograph of a larger particle of alloy C. Figure 5c and d are X-ray maps in the same field of V and Ni, respectively. The particle sizes of alloy C powders are around 5-12 μm . The pow-

der surface of alloy C (Fig. 5 b) looks concavo-convex which should be a more activated amorphous surface with a high catalytic activity. The V and Ni concentrations in alloy C are fairly evenly distributed, showing that the alloy C has a homogenous amorphous $\text{MgNiV}_{0.1}$ component and indicating that the MM nonstoichiometric Mg-based alloy can achieve a uniform amorphous structure.

The discharge capacities of the alloys A, C, D, E, and F after repeated charge-discharge cycles at a discharge current density of 50 mA/g are shown in Fig. 6. The discharge capacities were calculated based on the total weight of the alloys. Compared with the discharge capacity of the amorphous stoichiometric alloy A (336 mAh/g), the nonstoichiometric alloys C, D, E, and F have higher discharge capacities and better cycle characteristics. The initial discharge capacities of alloys C, D, E, and F are 414, 357, 361, and 362 mAh/g, respectively. The nonstoichiometric alloys D, E, and F have almost the same discharge capacity and cycle life, while alloy C has the highest discharge capacity and best cycle life. This shows that nonstoichiometric additions of vanadium can increase both the discharge capacity and cycle life of amorphous MgNi alloy electrodes, and that the amorphous MgNi alloy containing 0.1 molar addition of vanadium has the best electrode properties. These initial discharge capacities are higher than those of AB_5 -type and AB_2 -type hydride electrodes. Increasing the V content did not alter the electrode properties of the amorphous MgNi alloys. If the discharge capacities of the alloys are calculated based on Mg_2Ni content,⁵⁻⁸ the capacity of alloy C will be 658 mAh/g at a discharge current density of 79 mA/g. The nonstoichiometric addition of vanadium and nickel in MgNi

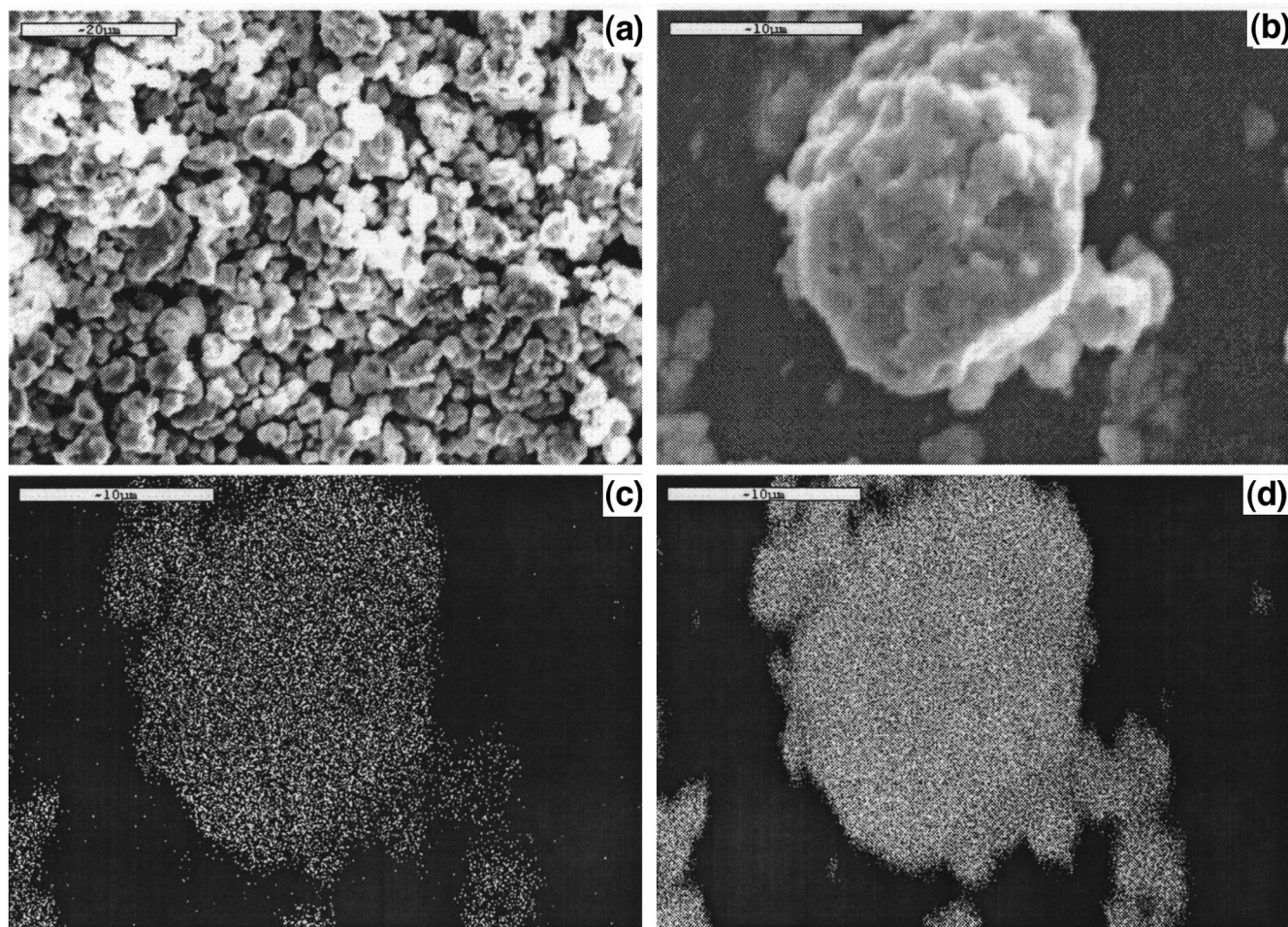


Figure 5. SEM micrograph of (a) the $\text{MgNiV}_{0.1}$ alloy powders. (b) The micrograph of a larger particle of $\text{MgNiV}_{0.1}$ alloy, X-ray mapping of (c) V and (d) Ni of $\text{MgNiV}_{0.1}$ alloy in the same field, respectively.

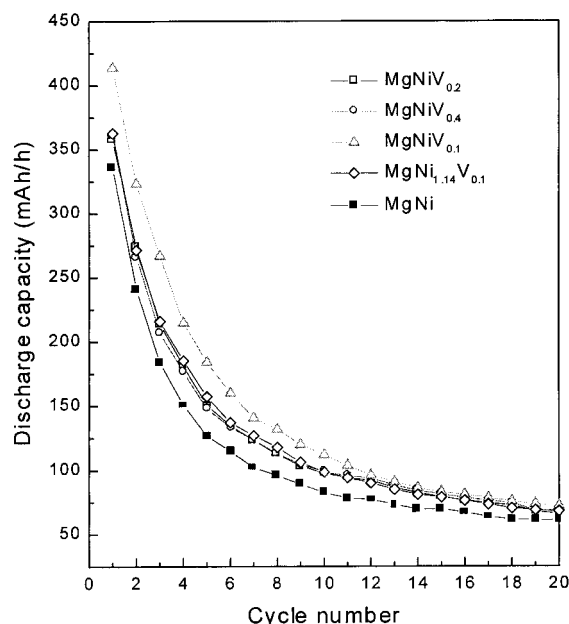


Figure 6. Discharge capacities of the alloys A, C, D, E, and F after repeated charge-discharge cycles at a discharge current density of 50 mA/g.

alloy cannot further increase its discharge capacity (alloy F) although it is still high (362mAh/g). Because amorphous alloys have excellent electrocatalytic activity,³⁴ all the nonstoichiometric amorphous Mg-based alloys have good hydriding/dehydriding kinetics at 25°C and high electrochemical hydrogen storage abilities. The discharge capacity degradation of all the nonstoichiometric Mg-based alloys is still fast due to the oxidation of Mg in the KOH solution.¹ However, it is possible for amorphous Mg-based alloys to have longer cycle lives. Some previous results have shown that amorphous Mg-based alloys have good corrosion resistance.^{35,36}

In summary, the nonstoichiometric amorphous Mg-based alloys can be achieved by the MM method for a range of V additions. The nonstoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities. These results describe a novel method of achieving better Mg-based alloy electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of different element.

Conclusions

The nonstoichiometric uniform amorphous MgNi_xV_y alloys ($x = 1, 1.28; y = 0, 0.1, 0.2, 0.4$) have been successfully synthesized by mechanical alloying induction melting Mg_2Ni alloy, Ni and/or V powders based on a stoichiometric amorphous MgNi alloy component. The results indicate that nonstoichiometric amorphous Mg-based alloys can be obtained by either increasing the Ni content or adding a range of vanadium or both through the MM method. The nonstoichiometric Mg-based alloy electrodes studied have shown

improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a method of achieving better Mg-based alloy electrodes with high discharge capacities. The method enables a larger composition range to be achieved with a range of vanadium additions.

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References

1. Y. Q. Lei, Y. M. Wu, Q. M. Yang, J. Wu, and Q. D. Wang, *Z. Phys. Chem.*, **183**, 379 (1994).
2. D. L. Sun, Y. Q. Lei, W. H. Liu, J. J. Jiang, J. Wu, and Q. D. Wang, *J. Alloys Compd.*, **231**, 621 (1995).
3. W. H. Liu, H. Q. Wu, Y. Q. Lei, Q. D. Wang, and J. Wu, *J. Alloys Compd.*, **261**, 289 (1997).
4. S. Nohara, K. Hamasaki, S. G. Zhang, H. Inoue, and C. Iwakura, *J. Alloys Compd.*, **280**, 104 (1998).
5. T. Kohno, S. Tsuruta, and M. Kanda, *J. Electrochem. Soc.*, **143**, L198 (1996).
6. T. Kohno and M. Kanda, *J. Electrochem. Soc.*, **144**, 2384 (1997).
7. S. Nohara, N. Fujita, S. G. Zhang, H. Inoue, and C. Iwakura, *J. Alloys Compd.*, **267**, 76 (1998).
8. C. Iwakura, H. Inoue, S. G. Zhang, and S. Nohara, *J. Alloys Compd.*, **270**, 142 (1998).
9. L. Sun, H. K. Liu, D. H. Bradhurst, and S. X. Dou, *Electrochem. Solid-State Lett.*, **2**, 164 (1999).
10. L. Sun, Y. Pei, H. K. Liu, D. H. Bradhurst, and S. X. Dou, *J. Alloys Compd.*, **293**, 536 (1999).
11. C. C. Han, J. J. Jiang, J. G. Park, K. J. Jang, E. Y. Chin, and J. Y. Lee, *J. Alloys Compd.*, **285**, L8 (1999).
12. J. H. Woo and K. S. Lee, *J. Electrochem. Soc.*, **146**, 819 (1999).
13. S. Orimo, K. Ikeda, H. Fujii, Y. Fujikawa, Y. Kitano, and K. Yamamoto, *Acta Mater.*, **45**, 2271 (1997).
14. J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.*, **7**, 2254 (1968).
15. W. Buckel and R. Hilsh, *Z. Phys.*, **138**, 109 (1954).
16. P. Duwez, R. H. Willens, and W. Klement, Jr., *J. Appl. Phys.*, **31**, 1136 (1960).
17. H. S. Chen, *Rep. Prog. Phys.*, **43**, 353 (1980).
18. *Amorphous Metallic Alloys*, F. E. Luborsky, Editor, Butterworths, London (1983).
19. *Glassy Metals*, H. J. Guntherodt and H. Beck, Editors, Springer-Verlag, Berlin (1981).
20. *Materials Science of Amorphous Metals*, T. Masumoto, Editor, Ohm Pub., Tokyo (1992).
21. *Rapidly Solidified Alloys*, H. H. Liebermann, Editor, Marcel Dekker Inc., New York (1993).
22. C. C. Koch, O. B. Cavin, C. G. Mckamey, and J. O. Scorbrough, *Appl. Phys. Lett.*, **43**, 1017 (1983).
23. W. L. Johnson, *Prog. Mater. Sci.*, **30**, 81 (1986).
24. K. Samwer, *Phys. Rev.*, **161**, 1 (1988).
25. L. Schultz, *Mater. Sci. Eng., A*, **97**, 15 (1988).
26. R. B. Schwarz, *Mater. Sci. Eng., A*, **97**, 71 (1988).
27. A. W. Weeber and H. Bakker, *Physica B*, **153**, 93 (1988).
28. C. C. Koch, *J. Non-Cryst. Solids*, **117/118**, 670 (1990).
29. T. Benamer and A. Inoue, *Mater. Trans. JIM*, **36**, 240 (1995).
30. H. J. Fecht, *Mater. Trans. JIM*, **36**, 777 (1995).
31. C. C. Koch, *Scr. Metall. Mater.*, **34**, 21 (1996).
32. J. Eckert, *Mater. Sci. Eng., A*, **226**, 364 (1997).
33. P. Y. Lee and C. C. Koch, *J. Non-Cryst. Solids*, **94**, 88 (1987).
34. K. Hashimoto, *Mater. Sci. Eng., A*, **226**, 891 (1997).
35. M. S. Ong, Y. Li, D. J. Blackwood, S. C. Ng, and C. H. Kam, *J. Alloys Compd.*, **270**, 142 (1998).
36. C. H. Kam, Y. Li, S. C. Ng, A. Wee, J. S. Pan, and H. Jones, *J. Mater. Res.*, **14**, 1638 (1999).