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Gaseous and Electrochemical Hydrogen Storage Properties of Nanocrystalline Mg_2Ni-Type Alloys Prepared by Melt Spinning

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ABSTRACT

A partial substitution of Ni by Cu has been carried out in order to improve the hydrogen storage characteristics of the Mg_2Ni-type alloys. The nanocrystalline $Mg_{20}Ni_{10-x}Cu_x$ (x = 0, 1, 2, 3, 4) alloys are synthesized by the melt-spinning technique. The structures of the as-cast and spun alloys have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM). The electrochemical performances were evaluated by an automatic galvanostatic system. The hydrogen absorption and desorption kinetics of the alloys were determined by using an automatically controlled Sieverts apparatus. The results indicate that the substitution of Cu for Ni does not alter the major phase Mg_2Ni. The Cu substitution significantly ameliorates the electrochemical hydrogen storage performances of alloys, involving both the discharge capacity and the cycle stability. The hydrogen absorption capacity of alloys has been observed to be first increase and then decrease with an increase in the Cu contents. However, the hydrogen desorption capacity of the alloys exhibit a monotonous growth with an increase in the Cu contents.

***Keywords*:** *Mg_2Ni-Type Alloy*, *Cu Substitution*, *Melt Spinning*, *Hydrogen Storage Property*

1. Introduction

Mg and Mg-based alloys in the form of metallic hydrides such as MgH_2 and Mg_2NiH_4 have been considered as potential materials for solid state hydrogen storage. The theoretical hydrogen storage capacities of MgH_2 and Mg_2NiH_4 are 7.6 wt% and 3.6 wt% [1,2] respectively. Unfortunately, the applications of this kind of materials are marred by their poor sorption/desorption kinetics and high dissociation temperature. Therefore, during the recent years, the main focus of research in this area has been to find the ways to substantially ameliorate the hydration kinetics of Mg-based alloys. In the past, various efforts such as mechanical alloying (MA) [3], GPa hydrogen pressure method [4], melt spinning [5], gravity casting [6], hydriding combustion synthesis [7], surface modification [8], alloying with other elements [9,10], and adding catalysts [11] have been undertaken to improve the activation and hydriding properties.

Zaluska *et al.* [12] have demonstrated the excellent absorption/desorption kinetics of a milled mixture of Mg_2NiH_4 and MgH_2 at 220-240˚C and claimed a maximum hydrogen concentration of more than 5 wt%. Hanada *et al.* [13] have reported a hydrogen storage capacity of 6.5 wt% after doping of MgH_2 with nanosized-Ni in a temperature range of 150-250˚C. Recham *et al.* [14] have concluded that the hydrogen absorption characteristics of ball-milled MgH_2 can be enhanced by adding NbF_5, and MgH_2 + NbF_5 composite has been found to desorb 3 wt% H_2 at 150˚C. Dobrovolsky *et al.* [15] have synthesized a MgH_2 (50 wt%) + TiB_2 (50 wt%) composite by intensive mechanical milling and found that TiB_2 additions lower the dissociation temperature of the MgH_2 hydride by about 50˚C. The results reported by Cui *et al.* [16] have testified the capability of amorphous and/or nanocrystalline Mg–Ni-based alloys to electrochemically absorb and also desorb a large amount of hydrogen at ambient temperatures. Kohno *et al.* [17] have documented a large discharge capacity of 750 mA·h/g at a current density of 20 mA/g for modified Mg_2Ni alloys.

Ball-milling indubitably is a very effective method for the fabrication of nanocrystalline and amorphous Mg and Mg-based alloys. Particularly, it is quite appropriate to solubilize the particular elements into MgH_2 or Mg_2NiH_4 above the thermodynamic equilibrium limit. This may facilitate the destabilization of MgH_2 or Mg_2NiH_4 [18]. However, the milled Mg and Mg-based alloys exhibit very poor hydrogen absorbing and desorbing stability on account of the evanishment of the metastable structures formed by ball milling during the multiple hydrogen absorbing and desorbing cycles [19]. Alternatively, the melt-spun technique has not only overcome the aforementioned shortcoming but also prohibits the significant degradation of the hydrogen absorbing and desorbing cyclic characteristics of Mg and Mg-based compounds [20]. Furthermore, the melt-spinning technique is a beneficial method to yield a nanocrystalline structure and has been regarded to be the most appropriate for the mass-production of the nanocrystalline Mg-based alloys. It has also been testified that the nanocrystalline alloys produced by melt-spinning method can exhibit excellent hydriding characteristics even at ambient temperatures, which is similar to that of the alloys fabricated by the MA process. Spassov *et al.* [21] have prepared Mg_2 (Ni, Y) hydrogen storage alloy with possessing the composition of $Mg_{63}Ni_{30}Y_7$ by rapid solidification process to yield a maximum hydrogen absorption capacity of about 3.0 wt%. In addition, the hydrogenation kinetics of the melt-spun Mg_2 (Ni, Y) have been observed to exceed those of the conventionally prepared polycrystalline Mg_2Ni alloys and also found to be comparable to that of the nanocrystalline ball-milled Mg_2Ni. Huang *et al.* [22] have concluded that the amorphous and the nanocrystalline Mg-based alloy $(Mg_{60}Ni_{25})_{90}Nd_{10}$ prepared by melt-spinning technique displays the highest discharge capacity of 580 mAh/g and the maximum hydrogen capacity of 4.2 wt% H.

Our previous work has confirmed that the substitution of Co for Ni significantly improves the hydriding and dehydriding kinetics of the Mg_2Ni-type alloys [23]. Therefore, it is very desirable to investigate the influence of substituting the Ni with Cu on the hydrogen storage characteristics of Mg_2Ni-type alloys prepared by melt-spinning. The objective of present work is to synthesize the Mg-Ni-based ternary nanocrystalline alloys by melt spinning and to examine their structures and hydrogen storage characteristics.

2. Experimental

The nominal compositions of the experimental alloys were $Mg_{20}Ni_{10-x}Cu_x$ (x = 0, 1, 2, 3, 4). For convenience, the alloys were denoted with Cu content as Cu_0, Cu_1, Cu_2, Cu_3 and Cu_4, respectively. The alloy ingots were prepared using a vacuum induction furnace in a helium atmosphere at a pressure of 0.04 MPa. A part of the as-cast alloys was re-melted and spun by melt-spinning with a rotating copper roller. The spinning rate was approximately expressed by the linear velocity of the copper roller because it was too difficult to measure a real spinning rate *i.e.* the cooling rate of the sample during spinning. The spinning rates used in the experiment were 15, 20, 25 and 30 m/s.

The phase structures of the as-cast and spun alloys were determined by XRD (D/max/2400). The diffraction, with the experimental parameters of 160 mA, 40 kV and 10˚/min was performed with $CuK_{\alpha 1}$ radiation filtered by graphite. The morphologies of the as-cast alloys were examined by SEM (Philips QUANTA 400). The thin film samples of the as-spun alloys were prepared by ion etching for observing the morphology with HRTEM (JEM-2100F, operated at 200 kV), and for determining the crystalline state of the samples with electron diffraction (ED).

The alloy ribbons were pulverized and then mixed with carbonyl nickel powder in a weight ratio of 1:4. The mixture was cold pressed into round electrode pellets of 10 mm in diameter and total mass of about 1 g with a pressure of 35 MPa. A tri-electrode open cell, consisting of a metal hydride electrode, a sintered $NiOOH/Ni(OH)_2$ counter electrode and a Hg/HgO reference electrode, was used for testing the electrochemical characteristics of the experimental alloy electrodes. A 6 M KOH solution was used as electrolyte. The voltage between the negative electrode and the reference electrode was defined as the discharge voltage. In every cycle, the alloy electrode was first charged at a current density of 20 mA/g, after resting for 15 min, it was discharged at the same current density to −0.500 V cut-off voltages. The environment temperature of the measurement was kept at 30˚C.

The hydrogen absorption and desorption kinetics of the alloys were monitored by an automatically controlled Sieverts apparatus. The hydrogen absorption was conducted at 1.5 MPa and the hydrogen desorption at a pressure of 1×10^{-4} MPa was performed at 200˚C.

3. Results and Discussion

3.1. Microstructure Characteristics

The XRD profiles of the as-cast and spun $Mg_{20}Ni_{10-x}Cu_x$ (x = 0-4) alloys are presented in **Figure 1**. The results indicate that all the as-cast and spun alloys display a single phase structure. The substitution of Cu for Ni does not modify the phase structure. **Table 1** lists the lattice parameters, cell volume and full width at half maximum

Table 1. The lattice parameters, cell volume and the FWHM values of the major diffraction peaks of the alloys.

Alloys	FWHM values				Lattice parameters and cell Volume					
	2θ (20.02°)		2θ (45.14°)		a (nm)		c (nm)		V (nm^3)	
	As-cast	15 m/s	As-cast	15 m/s	As-cast	15 m/s	As-cast	15 m/s	As-cast	15 m/s
Cu_0	0.122	0.125	0.169	0.171	0.5210	0.5210	1.3244	1.3251	0.3113	0.3115
Cu_1	0.133	0.155	0.178	0.194	0.5210	0.5212.	1.3252	1.3259	0.3115	0.3120
Cu_2	0.148	0.181	0.183	0.207	0.5214	0.5216	1.3283	1.3293	0.3127	0.3132
Cu_3	0.151	0.197	0.192	0.215	0.5215	0.5217	1.3297	1.3305	0.3132	0.3135
Cu_4	0.165	0.232	0.204	0.241	0.5217	0.5220	1.3302	1.3311	0.3135	0.3141

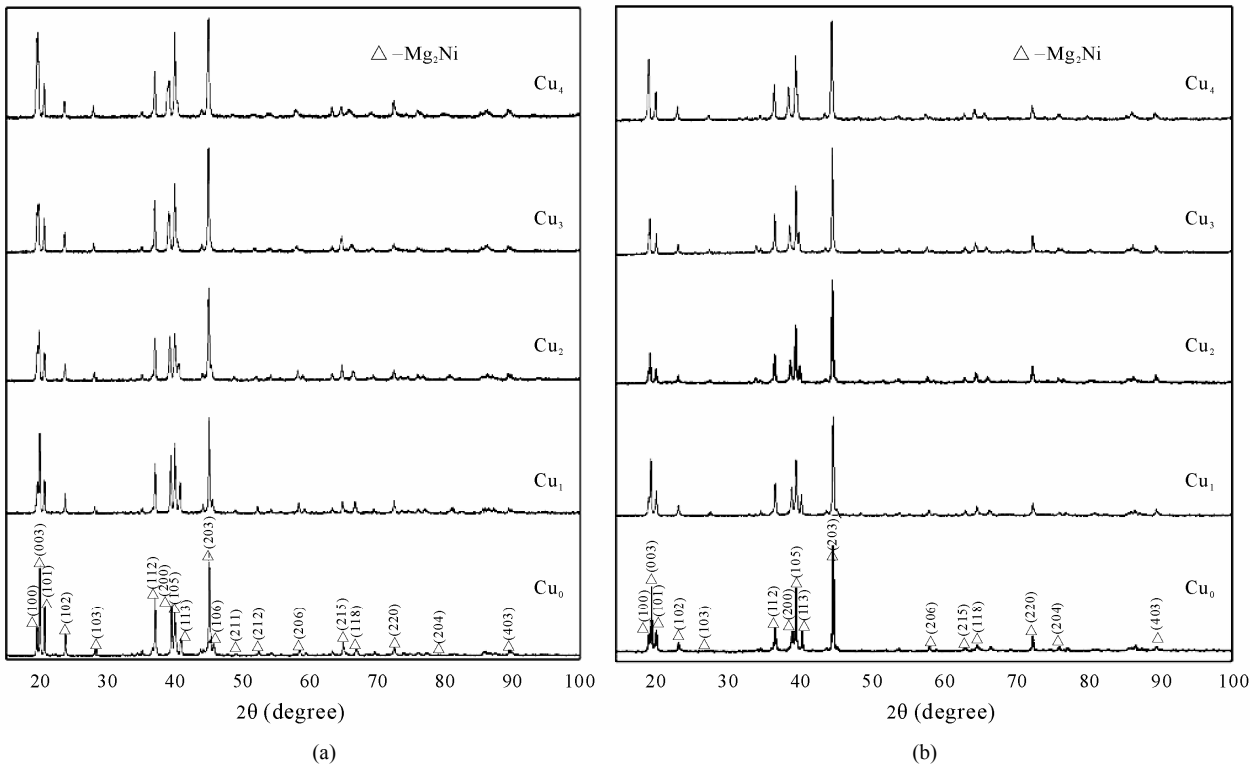


Figure 1. XRD profiles of the as-cast and spun alloys: (a) As-cast; (b) As-spun (15 m/s).

(FWHM) values of the main diffraction peaks of the as-cast and spun (15 m/s) alloys, which are calculated by software Jade 6.0. It is evident in **Table 1** that the substitution of Cu for Ni intensifies the FWHM values of the main diffraction peaks exhibited by the as-cast and spun alloys. Furthermore, it leads to a sharp enlargement of the lattice parameter and cell volume of the alloys, justifies the successful alloying of Cu with Mg_2Ni. **Table 1** also demonstrates the enhancement in the FWHM values of the main diffraction peaks of the alloys caused by the melt spinning, which is ostensibly attributed to the refinement of grains and the accumulated stress in grains rendered by the melt spinning. The crystallite size $\langle D_{hkl} \rangle$ (nm) of the as-spun alloy has been calculated by utilizing the FWHM values of the broad diffraction peak (203) in **Figure 1(b)** by employing the Scherer's equation. The grain size of the as-spun alloys is found to be in the range of 15-30 nm, which is consistent with the results reported by Friedlmeier *et al.* [24]. It is noteworthy that for the comparison purposes, the $\langle D \rangle$ values have been calculated by using the similar peak having the Miller indices (203).

The SEM images of the as-cast Cu_0 and Cu_2 alloys are illustrated in **Figure 2**. It is quite evident that the as-cast

alloys exhibit a typical dendritic structure. The substitution of Cu for Ni, instead of changing the morphology of the alloys, causes a significant refinement of the grains. The result obtained by energy dispersive spectrometry (EDS) reveals that the major phase of the as-cast alloys is Mg_2Ni phase (denoted by A). The Cu_2 alloy clearly exhibits some small massive particulates. The EDS analysis confirms that these particulates are Mg_2Cu phase (denoted by B). This result is contrary to the XRD observations depicted in **Figure 1**. This phenomenon may be attributed to the fact that the amount of the Mg_2Cu phase is very little and therefore unable to be detected by the XRD observation.

Figure 3 depicts the TEM micrographs and electron diffraction patterns of as-spun Cu_0 and Cu_2 alloys. A nanocrystalline microstructure possessing an average crystal size of about 20 nm is evident. TEM observations clearly supplement the evidence of the presence of strongly disordered and nanostructured phase of as-spun alloys. This result agrees very well with the XRD observations shown in **Figure 1**.

The existence of crystal defects in the as-spun alloy such as stacking faults (denoted as A), dislocations (denoted as B), sub-grain boundaries (denoted as C) and twin-grain boundaries (denoted as D) is clearly depicted in **Figure 4**.

3.2. Electrochemical Hydrogen Storage Performances

3.2.1. Activation Capability and Discharge Capacity

Electrochemical galvanostatic charge/discharge is an effective and time-saving method for determining the hydrogen absorbing capacity as compared with a gaseous technique. The influence of substituting Ni with Cu on

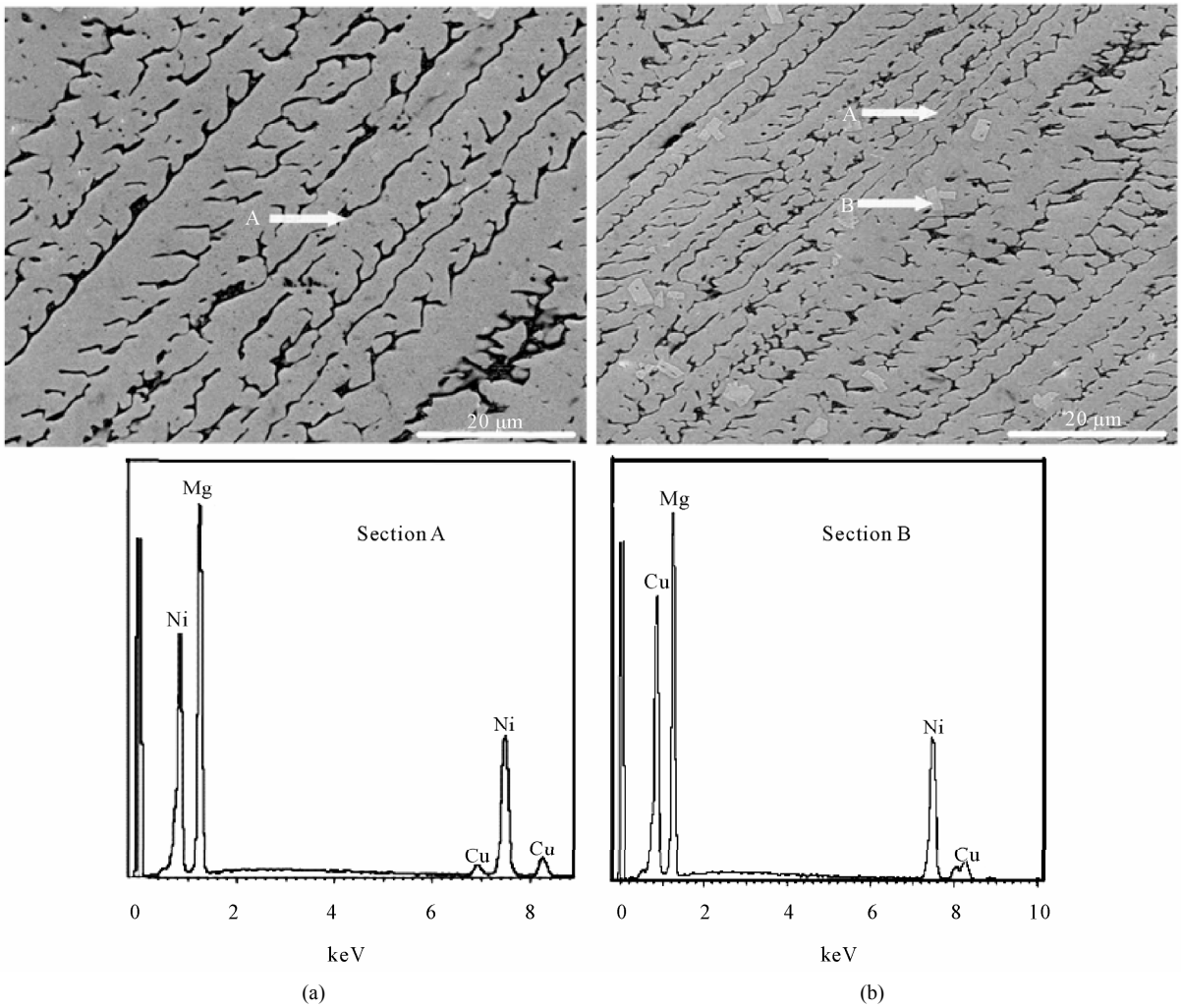
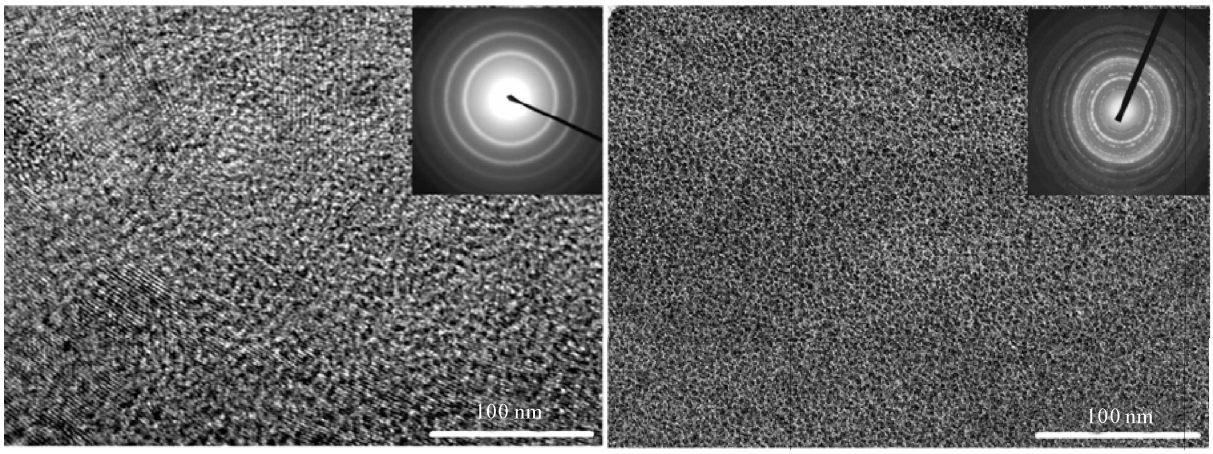
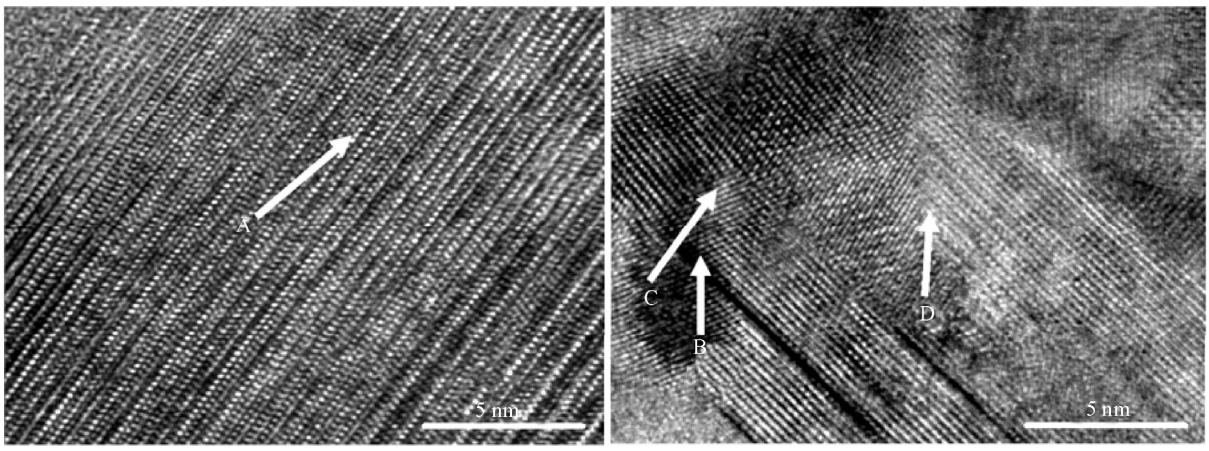


Figure 2. SEM images of the as-cast alloys together with typical EDS spectra of sections A and B in Figure 2(b): (a) Cu_0 alloy; (b) Cu_2 alloy.



(a) (b)

Figure 3. HRTEM micrographs and ED of the as-spun alloys (30 m/s): (a) Cu_0 alloy; (b) Cu_2 alloy.



(a) (b)

Figure 4. Crystal defects in the as-spun (30 m/s) Cu_2 alloy taken by HRTEM: (a) Stacking fault; (b) Dislocations, sub-grain boundaries and twin-grain boundary.

the activation capability of the alloys with a charging-discharging current density of 20 mA/g is shown in **Figure 5**. The figure demonstrates that all the alloys exhibit excellent activation capability and attains their maximum discharge capacities during the first charging-discharging cycle. The activation performances of the alloys are not affected by the substitution of Cu for Ni. The discharge capacity of the as-spun alloys first increases and then decreases with the variation of Cu content. The Cu_2 alloy presents the maximum discharge capacities of 135.8 mAh/g and 189.3 mAh/g corresponding with two spinning rates of 20 m/s and 30 m/s, respectively. It must be mentioned that the discharge capacity of alloys substituted by Cu is higher than that of the Cu-free alloy, suggesting that the substitution of Cu for Ni has ameliorated the discharge capacity of Mg_2Ni-type alloy. A similar result has already been reported by Simičić *et al.* [2]. The specific capacity and hydriding/dehydriding kinetics of hydride electrode materials depend on their chemical composition and crystalline structure. It has been ascertained that the high hydride formation enthalpy of Mg_2Ni accounts for its low discharge capacity. The partial substitution of some elements (Cu, Fe, V, Cr, Co) for Ni in Mg_2Ni compound may facilitate the destabilization of the hydride and activate the Mg_2Ni phase to exhibit the reversible hydrogen storage properties in the alkaline electrolyte [25]. On the other hand, the secondary phase Mg_2Cu probably acts as an efficient catalyst to dissociate the H_2 molecules and transferring the H atoms to the surrounding Mg_2Ni matrix [19].

3.2.2. Charging and Discharging Cycle Stability

The cyclic stability of the electrode alloy is a decisive factor in determining the life of Ni-MH battery. The ca-

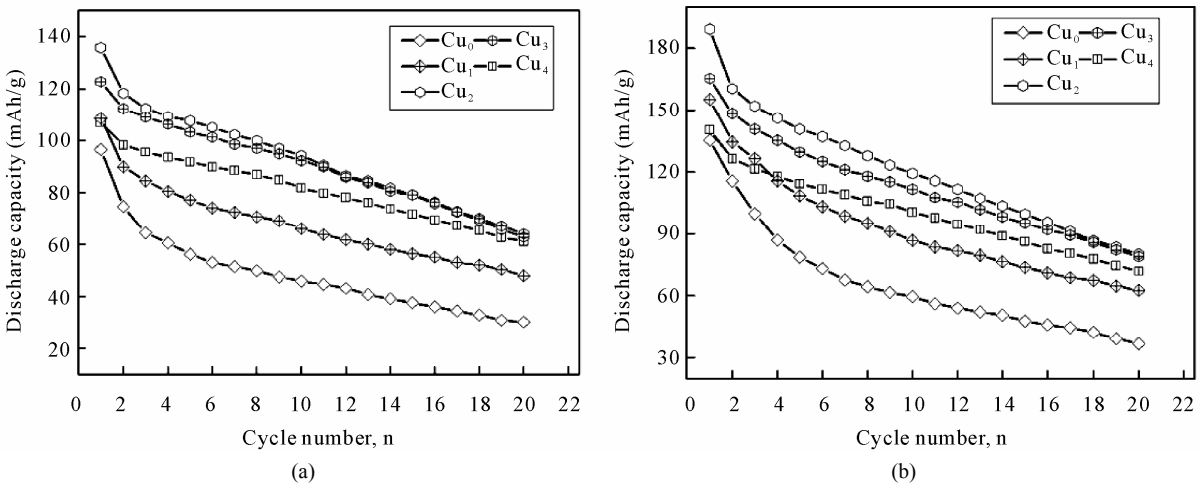


Figure 5. Evolution of the discharge capacity of the as spun alloys with the cycle number: (a) 20 m/s; (b) 30 m/s.

pacity retaining rate (S_n), which is introduced to evaluate accurately the cyclic stability of the alloy, is defined as $S_n = C_n/C_{max} \times 100\%$, where C_{max} is the maximum discharge capacity and C_n is the discharge capacity of the nth charge-discharge cycle. It has been observed that the large capacity retaining rate (S_n) yields in the better cycle stability of the alloy. The capacity retaining rates of as-spun alloys as a function of cycle number are plotted in **Figure 6**. The figure indicates that the substitution of Cu for Ni has significantly enhanced the cyclic stability of as-spun alloys. As the Cu contents x grow from 0 to 4, the capacity retaining rate of the as-spun (20 m/s) alloy at 20th cycle increases from 31.3 to 57.2%, and from 27.1 to 51.1% for the as-spun (30 m/s) alloy. It is well known fact that the main rationale for the capacity degradation of Mg-based alloy electrodes is the severe corrosion of Mg in the alkaline KOH solution. Especially, during the discharging process, the anodicpolarization of alloys facilitates the faster corrosion rate [25]. On the other hand, the vanishment of metastable structures formed by melt spinning or ball milling during the multiple charging/ discharging cycles tend to enhance the capacity decay of the alloys. Two reasons are responsible for the enhanced cyclic stability of the Mg_2Ni-type alloy subjected with Cu substitution. Firstly, the improved performance regarding the cyclic life of substituted alloy electrode is presumably attributed to preferential oxidation of Cu on the alloy surface, which prevents the formation of $Mg(OH)_2$ passive layer. Secondly, the additions of a third element significantly stabilize the nanostructure formation of Mg-Ni-based alloy [21], suggesting an increase of the cyclic stability of alloy. Furthermore, the comparison of **Figures 6(a)** and **(b)** reveals that the capacity retaining rates of alloys slightly decline with rising spinning rate. It implies that the melt spinning mildly impairs the cyclic stability of alloys. The nanostructure exhibiting by the alloys resulting from melt spinning has been considered to be detrimental due to its corrosion in the electrolyte during cycling on account of the fact that the intercrystalline corrosion is facilitated by the nanostructure formation. This provides an illustration for the decline of the cyclic stability of the Mg-Ni-Cu system alloy caused by a higher spinning rate.

3.3. Hydriding and Dehydriding Characteristics

The hydrogen absorption kinetic curves of the as-spun alloys are depicted in **Figure 7**. It is evident that the hydrogen absorption capacity of the as-spun alloys first increases and then decreases with the variation of Cu content. The Cu_2 alloy demonstrates the maximum hydrogen absorption capacity at 200˚C. The evidence of extremely fast kinetics of hydrogenation is provided by the fact that the alloys acquire more than 95% of their hydrogen capacities within the first 5 min. The excellent hydriding kinetics is ascribed to the nanocrystalline structure resulting in the high surface to volume ratios (high specific surface area). In addition, the presence of large number of grain boundaries in nanocrystalline alloys enhances the kinetics of hydrogen absorption/desorption. The benefaction of Cu substitution on the hydrogen absorption capacity and kinetics of the alloy has also been attributed to the increased cell volume and the refined grain caused by Cu substitution. The enlargement in the cell volume is highly beneficial to the hydrogen absorption capacity, since, the grain boundary possesses the capability of the largest hydrogen absorption [25]. It is well known that the catalytic action of Ni on hydriding is stronger than Cu. Therefore, it is justifiable that a superfluous amount of Cu substitution ($x > 2$) leads to a decrease of the hydrogen absorption capacity of the al-

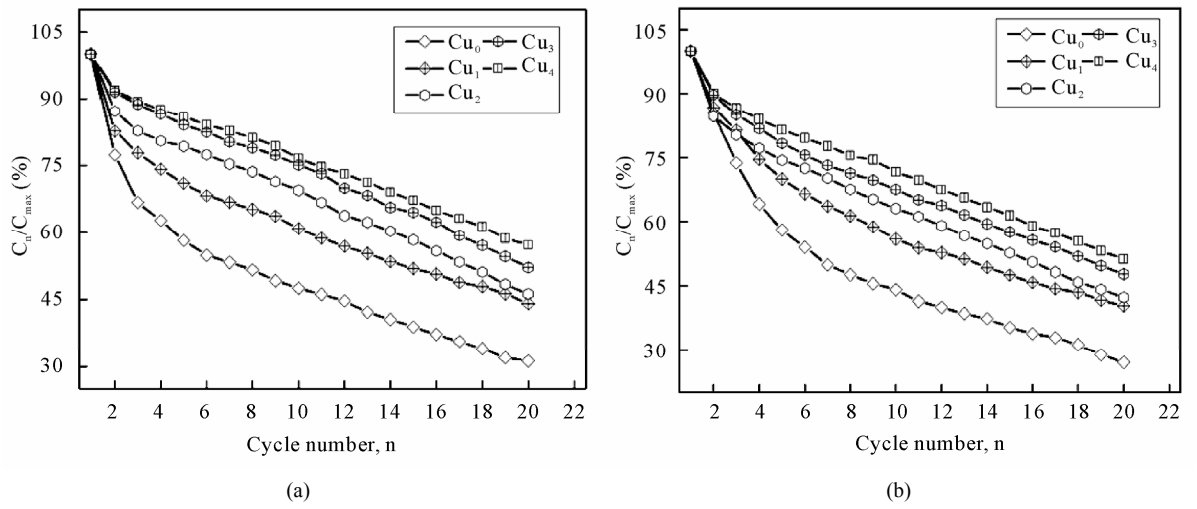


Figure 6. Evolution of the capacity retaining rate of the alloys with cycle number: (a) 20 m/s; (b) 30 m/s.

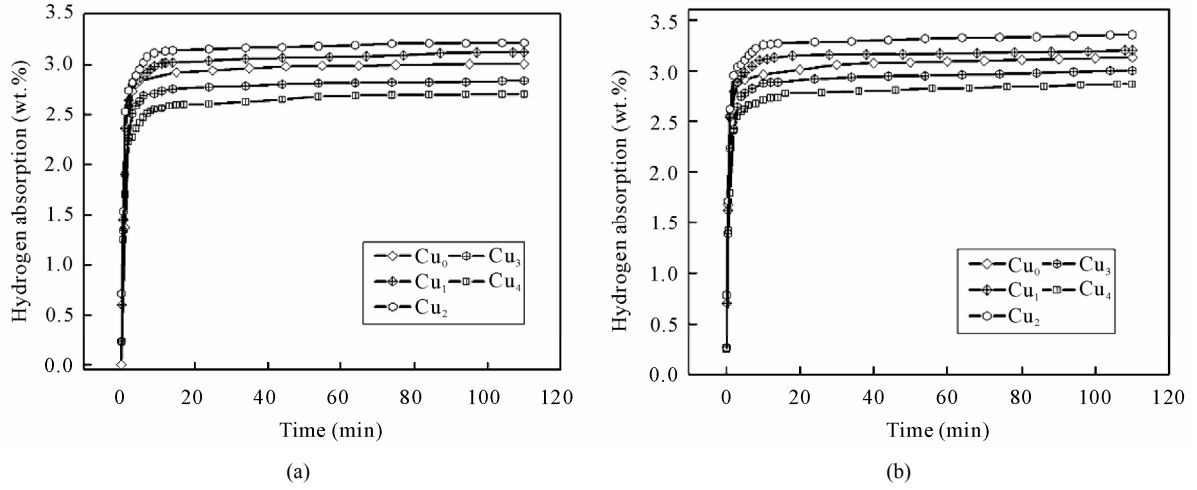


Figure 7. Hydrogen absorption kinetic curves of the as-spun alloys: (a) 20 m/s; (b) 30 m/s.

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The hydrogenation kinetics and storage capacity of all the as-spun nanocrystalline Mg_2Ni-type alloys have been found to be superior to those of conventional polycrystalline materials possessing the similar composition. The enhanced hydrogenation property generated by melt spinning is doubtlessly associated with the refinement of grains produced by melt spinning [26]. Upon refining the microstructure, a lot of new crystallites and grain boundaries evolve, which may act as fast diffusion paths for hydrogen absorption.

The hydrogen desorption kinetic curves of the as-spun alloys are plotted in **Figure 8**. An essential characteristic of the dehydrogenation process in the alloys is very fast hydrogen desorption at the initial stages, followed by a slack increase in the amount of hydrogen absorbed. The specific capacity and hydriding/dehydriding kinetics of hydride materials depend on their chemical composition and crystalline structure [27]. The observed differences from the previous documented results about the hydriding/dehydriding kinetics of the melt-spun nanocrystalline Mg_2Ni type alloys may be associated with the composition of alloys, whereas, the differences in their microstructure may be ascribed to the various spinning rates. It has been already reported that the high surface to volume ratios (high specific surface area) and the existence of large number of grain boundaries in nanocrystalline alloys enhance the kinetics of hydrogen absorption/desorption [21]. Zaluski *et al.* [28] and Orimo *et al.* [29] have confirmed the exhibition of low temperatures (lower than 200˚C) hydriding/dehydriding characteristics of nanocrystalline Mg_2Ni alloys prepared by mechanical al-

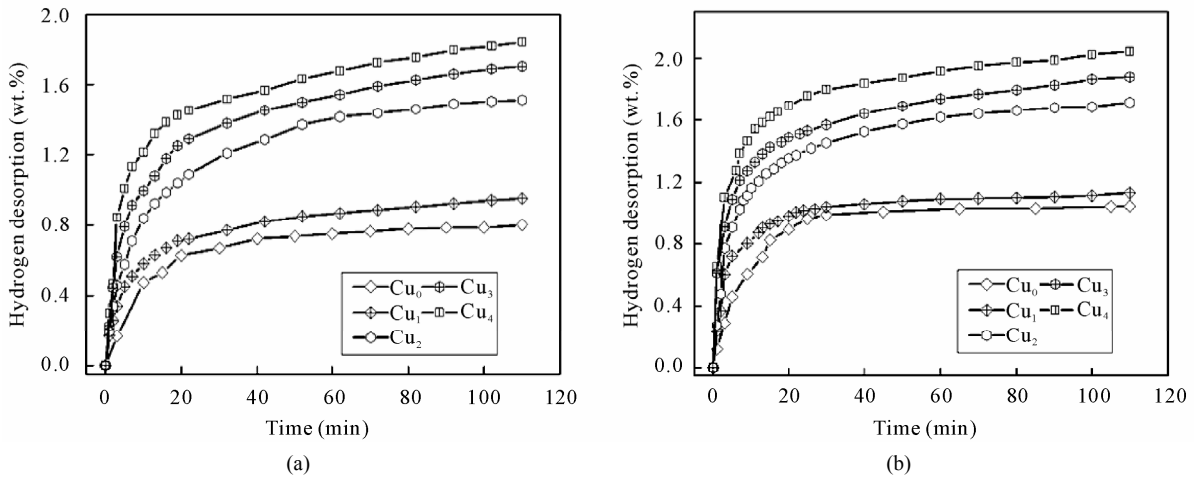

Figure 8. Hydrogen desorption curves of the as-spun alloys: (a) 20 m/s; (b) 30 m/s.

loying. They have testified that a reduction in the grain size (20-30 nm) enhances the hydriding/dehydriding characteristics owing to the hydrogen occupation in the disordered interface phase. Two reasons are chiefly responsible for the impact action of Cu substitution on the dehydriding kinetics of the alloys. Firstly, the partial substitution of element Cu for Ni in Mg_2Ni compound weakens the stability of hydride and renders the desorption reaction easier [30]. Secondly, the presence of Mg_2Cu phase apparently presents the catalytic effects for the hydriding and dehydriding reactions of Mg and Mg-based alloys [19].

4. Conclusions

1) All the as-spun $Mg_{20}Ni_{10-x}Cu_x$ (x = 0, 1, 2, 3, 4) alloys exhibit the nanocrystalline structures without showing any presence of amorphous phase. The substitution of Cu for Ni does not vary the major phase of Mg_2Ni-type in the alloy. On the contrary, the substitution leads to a significant refinement of grains in the as-cast alloys.

2) The Cu substitution has significantly enhanced the electrochemical hydrogen storage performances of alloy. It ameliorates the discharge capacity and the cycle stability by lowering the stability of hydride. This improvement is mainly attributed to the enlargement in the cell volume and the refinement of grains caused by the Cu substitution.

3) Furthermore, the substitution of Cu for Ni renders the hydrogen absorption capacity of the alloys first increased and then decreased. But overall it enhances the hydrogen desorption capacity and dehydriding rate of the alloys.

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