The influence of Co content on LaNi3.2-xMn03Cox (x=0.2~0.8) Alloy Hydrogen Storage and Electrochemical Properties

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Abstract

The cold crucible levitation melting prepared LaNi3.2-xMn03Cox (x = 0.2 ~ 0.8) series alloys, the system of Co substitution of Ni on the alloy structure, hydrogen storage performance and electrochemical properties. XRD analysis showed that the cast alloy by the La2Ni7 phase, LaNi5 phase and LaNi3 phase composition; PCT test shows that with the Co substitution increases, the amount of the cast alloy of hydrogen first increased and then decreased, alloy hydrogen absorption and desorption plateau pressure changed little. Electrochemical tests show that as x increases the maximum discharge capacity of alloy electrodes decreases, the maximum discharge capacity Cmax by the x = 0.2 when 320.5mAh / g decreased to x = 0.8 when 286.6mAh / g, but the cycle stability significantly improved after 60 charge-discharge cycles, the alloy electrode capacity retention rate (S60) by the x = 0.2 and gradually increased to 72.9% when x = 0.8 at 84.9%.

Key words: A2B7-type; Hydrogen storage alloy; Electrochemical performance; Hydrogen storage performance

A2B7 AB5 type rare-earth alloy with a rare earth alloy is higher than the theoretical electrochemical capacity, but because of the existence of the phenomenon of hydrogen hydrogenation, resulting in the actual discharge capacity is far lower than the theoretical discharge capacity [1]. Our previous work studied LaNi3.0-xMnxCo0.5 (x = 0.1 ~ 0.5) quaternary alloys, studies have shown that partial substitution of Ni with Mn, the alloy in addition to the above x = 0.1, the electrochemical discharge capacity of the other alloys are higher than La2Ni7 binary alloy [2], electrochemical discharge capacity, and when at x = 0.3 show good overall performance, the discharge capacity of up to 327.3mAh / g, but the cycle stability need to be further improved. Is well known [3,4], in the AB5-type rare earth hydrogen storage electrode alloys, Co alloys is to improve the cycle stability of one of the most effective elements, Co Alloy B-side group of the partial substitution of Ni element can reduce the hardness of the alloy enhance the toughness of the alloy, reducing the volume expansion of alloy after hydrogenation to improve the alloy's resistance to chalking; the same time, the charge-discharge process, Co alloy can inhibit the surface Mn, Al and...
other elements of the dissolution, reducing the corrosion rate of alloy, which improve the alloy's cycle life. Therefore, in previous work based on the paper selected LaNi3.2-xMn0.3Cox (x = 0.2 ~ 0.8) quaternary alloy as the research object, the system of Co content on the phase structure of alloys, hydrogen storage and electrochemical properties affect the laws and mechanisms to further improve the alloy's overall performance.

1. Experimental

In Ar gas atmosphere protection, using cold crucible levitation melting prepared LaNi3.2-xMn03Cox (x = 0.2 ~ 0.8) series alloys. The purity of the metal materials used were higher than 99%. To ensure uniformity of alloy composition, the ingot remelting flip three times to get the cast alloy samples. The melting alloy after mechanical crushing good after over 200 mesh sieve, respectively, XRD, PCT performance tests and electrochemical performance testing.

Alloy phase structure of Japan Science D / MAX 2500V X-ray diffraction (40KV, 150mA of Cu target radiation, graphite monochromator) test, using Jade 5.0 software and alloy powder diffraction analysis of phase structure card. Hydrogen absorption and desorption properties of the alloy using JY-1 automatic PCT testers.

Alloy electrode performance DC-5 battery tester for testing, using computer control and experimental data acquisition. Nickel alloy powder and hydroxy mixed mass ratio of 1:4, the powder pellet machine to 20MPa pressure cold into thin round 10mm diameter alloy electrode as a test piece, weighing the pads, and follow the alloy the ratio of powder and nickel powder electrode chip to calculate the actual quality of hydrogen storage alloy, and then wrap and foam pads with pressure-type, and then with the spot together with nickel, as the test alloy electrodes. Alloy electrode performance testing in open-type H-glass three-electrode test systems, auxiliary electrode for the electrochemical capacity is much higher than the test alloy electrodes sintered nickel hydroxide electrode (Ni (OH) 2/NiOOH), reference electrode is made of mercury - mercury oxide (Hg / HgO) electrode, the electrolyte is 6mol / L KOH solution. Electrode charge and discharge parameters: the charging current density Ic = 100mA / g, the discharge current density Id = 80mA / g, the discharge cutoff voltage of 0.06V (relative to reference electrode). The experiment at room temperature.

2. Results and discussion

2.1 Crystal structure of the alloy

![Fig.1 XRD patterns of LaNi3.2-xMn0.3Cox hydrogen storage alloys](image-url)
Figure 1 shows the cast alloy LaNi3.2-xMn0.3Cox (x = 0.2 ~ 0.8) of the XRD patterns. It can be seen, with the x value increases, the alloy of the XRD patterns did not change significantly, the analysis shows, the cast alloy composed by the multi-phase, each phase were La2Ni7 phase, La (Ni, Co) 5 phase and LaNi3 phase. Table 1 lists the alloy in each phase of the cell parameters.

Table 1  Lattice parameters of the LaNi3.2-xMn0.3Cox (x=0.2~0.8) hydrogen storage alloys

| x   | Phases   | Space group      | Lattice Parameter/Å | Cell volume/Å³ |
|-----|----------|------------------|---------------------|---------------|
|     |          |                  | a                   | b             | c             |             |
| 0.  | La2Ni7   | P63/mmc (194)    | 5.06194             | 24.67395      | 547.53        |
| 2   | LaNi5    | P6/mmm (191)     | 5.01995             | 3.99746       | 87.24         |
|     | LaNi3    | R-3m (166)       | 5.03065             | 24.99335      | 547.78        |
| 0.  | La2Ni7   | P63/mmc (194)    | 5.07                | 24.60935      | 547.83        |
| 4   | LaNi5    | P6/mmm (191)     | 4.96757             | 4.01438       | 85.79         |
|     | LaNi3    | R-3m (166)       | 5.05792             | 24.60744      | 545.18        |
| 0.  | La2Ni7   | P63/mmc (194)    | 5.06578             | 24.47602      | 543.96        |
| 6   | LaNi5    | P6/mmm (191)     | 5.00205             | 4.01387       | 86.97         |
|     | LaNi3    | R-3m (166)       | 5.03116             | 24.8712       | 545.21        |
| 0.  | La2Ni7   | P63/mmc (194)    | 5.06719             | 24.5949       | 546.9         |
| 8   | LaNi5    | P6/mmm (191)     | 5.01223             | 4.01257       | 87.3          |
|     | LaNi3    | R-3m (166)       | 5.03599             | 24.89526      | 546.79        |

2.2 The PCT characteristics of alloys

Figure 2 shows the cast alloy LaNi3.2-xMn0.3Cox (x = 0.2 ~ 0.8) at 303K under the PCT curve of temperature, derived from the PCT curve of hydrogen storage alloy (maximum hydrogen absorption amount of hydrogen absorption and desorption plateau pressure, lag factor, etc.)
Table 2. It can be seen, with the Co substitution increases, the maximum hydrogen absorption capacity alloy first increases and then decrease when the x = 0.2 0.99 (wt%) gradually increased when x = 0.4 1.09 (wt%), followed by lower time for the x = 0.8 0.99 (wt%), which may be related alloys with various hydrogen abundances for. On the other hand, with the Co substitution increases, the alloy hydrogen plateau pressure were 0.3atm, 0.18atm, 0.18atm and 0.28atm, elements can be considered a partial substitute for Ni Co alloy system for hydrogen absorption and desorption plateau pressure has little effect this is because the atomic radius of Co (0.167nm) and Ni atomic radius (0.162nm) are similar, Co replaces Ni alloy after the main phase of the cell volume will remain basically unchanged. In addition, with the Co content increases, the hydrogen absorption alloy platform lag factor from 0.32 when x = 0.2 and gradually decreased to 0.21 when x = 0.8, the lag effect has been significantly improved, which may be enhanced with Co alloy toughness, to reduce hydrogenated alloy after volume expansion and reduces the hydrogen absorption alloy in the process of stress and strain related [5].

### Table 2 The H/M, Plateau pressure and Hf of LaNi₃.₂-xMn₀.₃Cox (x=0.₂~0.₈) alloys

| Sample | H/M (wt.%) | Plateau pressure(atm.) | Hf Log(Pa/Pd) |
|--------|------------|------------------------|---------------|
| x=0.2  | 0.99       | 0.62                   | 0.30          | 0.32          |
| x=0.4  | 1.09       | 0.35                   | 0.18          | 0.28          |
| x=0.6  | 1.05       | 0.32                   | 0.18          | 0.25          |
| x=0.8  | 0.99       | 0.45                   | 0.28          | 0.21          |

2.3 Electrochemical properties of alloy.

2.3.1 Activation performance and the maximum discharge capacity

LaNi₃.₂-xMn₀.₃Cox (x = 0.2 ~ 0.8) series alloys in the discharge current of 80mAh / g activated under the conditions shown in Figure 3, the activation frequency (Na) and the maximum discharge capacity (Cmax) in Table 3 shown. Figure 3 and Table 3 shows that all alloys after 3 to 4 times you can charge and discharge cycles to reach its maximum discharge capacity, showing good activation performance. With the Co content increases, the alloy by the maximum discharge capacity 320.5mAh / g (x = 0.2) gradually reduced to 286.6mAh / g (x = 0.8), the maximum discharge capacity of alloy electrode with Co content of the relationship shown in Figure 4.

![Fig.3 Activation profiles of the LaNi₃.₂-xMn₀.₃Cox (x=0.₂~0.₈) alloy electrodes](image-url)
Table 3 The Na and Cmax of the LaNi$_{3.2-x}$Mn$_{0.3}$Co$_x$ (x = 0.2~0.8) alloy electrodes

| Alloys   | x = 0.2 | x = 0.4 | x = 0.6 | x = 0.8 |
|----------|---------|---------|---------|---------|
| Na       | 3       | 3       | 3       | 4       |
| Cmax     | 320.5   | 312.2   | 302.3   | 286.6   |

Fig. 4 The effect of Co content on the Max discharge capacity (303 K)

Figure 5 LaNi$_{3.2-x}$Mn$_{0.3}$Co$_x$ (x = 0.2 ~ 0.8) alloy electrodes after full activation of the discharge curve, we can see, all the alloys have appeared on the discharge curve of a reflection of hydride hydrogen in the electro-chemical oxidation of the discharge voltage platform, with the Co content increases, the midpoint potential of the alloy discharge changed little.

Fig. 5 The discharge curves for the LaNi$_{3.2-x}$Mn$_{0.3}$Co$_x$ (x = 0.2~0.8) alloy electrodes at 303 K

2.3.2 Cycle stability
Figure 6 LaNi3.2-xMn0.3Cox (x = 0.2 ~ 0.8) alloy electrodes of the cyclical nature of the series of curves, the alloy electrodes after 60 cycles the capacity retention rate after the S60 as shown in Table 4. It can be seen, with the Co substitution increases, the capacity retention rate of the alloy x = 0.2 at S60 by the 72.9% when x = 0.8 and gradually increased to 84.9%, indicating a partial substitute for Ni Co alloy electrode after the cycling stability improved, mainly with hydrogen absorption alloy powder particles tend to reduce oxidation and corrosion of the alloy elements decreased activity of the [5], and rare earth in the AB5-type hydrogen storage alloys using Co partial substitution of Ni same conclusion [6].

Table 4 Evolution of the discharge capacity after 60 cycles for LaNi3.2-xMn0.3Cox (x=0.2~0.8) alloys

| Alloys | x=0.2 | x=0.4 | x=0.6 | x=0.8 |
|--------|-------|-------|-------|-------|
| S60(%) | 72.9  | 80.2  | 81.6  | 84.9  |

3.Conclusions

LaNi3.2-xMn0.3Cox (x = 0.2 ~ 0.8) and electrochemical hydrogen storage alloy for performance testing, you can get the following conclusions:

(1) by the multi-phase composition of cast alloy, each phase were La2Ni7 phase, La (Ni, Co) 5 phase and LaNi3 phase.

(2) Co substitution x increases, the amount of the cast alloy of hydrogen first increased and then decreased, alloy hydrogen absorption and desorption plateau pressure changed little.

(3) As x increases the maximum discharge capacity of alloy electrode decreases, Cmax by the x = 0.2 when 320.5mAh / g decreased to x = 0.8 when 286.6mAh / g. But the cycle stability improved significantly, after 60 charge-discharge cycles, the alloy electrode capacity retention rate (S60) by the x = 0.2 and gradually increased to 72.9% when x = 0.8 at 84.9%, mainly with the alloy particles hydrogen to reduce the tendency of powder and alloy active elements weakening of oxidative corrosion.

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