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Degradation mechanism of the misch metal alloy hydride electrodes

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Abstract

Pieces of nonpulverized misch metal (Mm) alloy were used as working electrodes (WEs). The WEs were cathodically charged in H_2 and O_2 atmospheres, respectively, and the electrode potentials were determined. The morphologies of definite areas of WEs were observed by SEM, and the surface composition in chemical elements of these areas were determined by EPMA. The results indicated that the main causes of the degradation of WEs might be the increase of internal stress, the expansion of crystal lattice, and the preferential dissolution of Mm during charging, rather than the oxidation of the alloy by O_2, which was accordant with the presence of La^{3+} and Ni^{2+} in the MH electrode of MH/Ni batteries after cycling.

Keywords: Degradation mechanism; Misch metal alloy; Electrode; MH/Ni batteries

1. Introduction

Misch metal (Mm) alloys used as negative electrode materials in MH/Ni batteries are noted for their inexpensiveness, and have been commercialized. However, these materials often shorten the cycle life of the batteries. Willems [1] showed that the cause of capacity decrease of $LaNi_5$ negative electrodes was the crystal lattice expansion and pulverization of the hydrogen storage alloy. Meli et al. [2] showed that chemical adsorption of oxygen resulted in the formation of $La(OH)_3$ and La_2O_3 on $LaNi_5$ surface. Boonstra et al. [3] showed that the formation of $La(OH)_3$ and $Ni(OH)_2$ resulted in the capacity decrease, with a ratio of $La(OH)_3:Ni(OH)_2=1:5$.

Multicomponent alloys were used to improve the cycle life of negative electrodes, but the real function of these alloys has not yet been ascertained, thus to clarify the degradation mechanism of Mm alloy hydride electrodes was the purpose of this work.

Pieces of nonpulverized Mm alloy ($MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$) were used as working electrodes (WEs). The WEs were cathodically charged in H_2 and O_2 atmosphere, respectively. The surface micromorphologies of specific areas on WEs were observed by SEM. The surface composition of WEs was determined by EPMA, and the potentials of WEs in a steady state were measured. The results showed that the main causes for the degradation of Mm alloy hydride electrodes were the increase of internal stress, the expansion of crystal lattice, and the preferential dissolution of Mm, rather than the oxidation of the alloy by oxygen.

2. Experimental details

Pieces of nonpulverized Mm alloy ($MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$) were processed by wire cutting, and machined into cylinders of 1-cm diameter and 0.5-cm height. Then a conducting wire was welded to the back of the sample. The cylinders' surfaces were sealed with epoxy resin except the working area, which was polished with $280^{\#}$, $600^{\#}$ and $1200^{\#}$ metallographic abrasive cloths successively until no obvious scratches were observed under a metallographic microscope with a magnification of 45×8. Then the cylinder was immersed in a 3% alcoholic solution of HNO_3 for 150 s. Finally, the cylinder (WE) was rinsed with tap water. The original surface morphology was observed by SEM, and some areas were defined, and the surface compositions of the same areas were determined by EPMA. Attention was paid to ensure all the examinations were made on the same areas of WEs.

The experimental system consisted of a WE, a nickel hydroxide counter electrode with much larger capacity than that of WE and a controlled atmosphere during discharge (either H_2 or O_2) and some nonwoven cloth as a separator. Hg/HgO/6 M KOH electrode was used as the reference one. H_2 or O_2 gas from a H_2 generator was made to flow continuously and separately through the partially sealed system.

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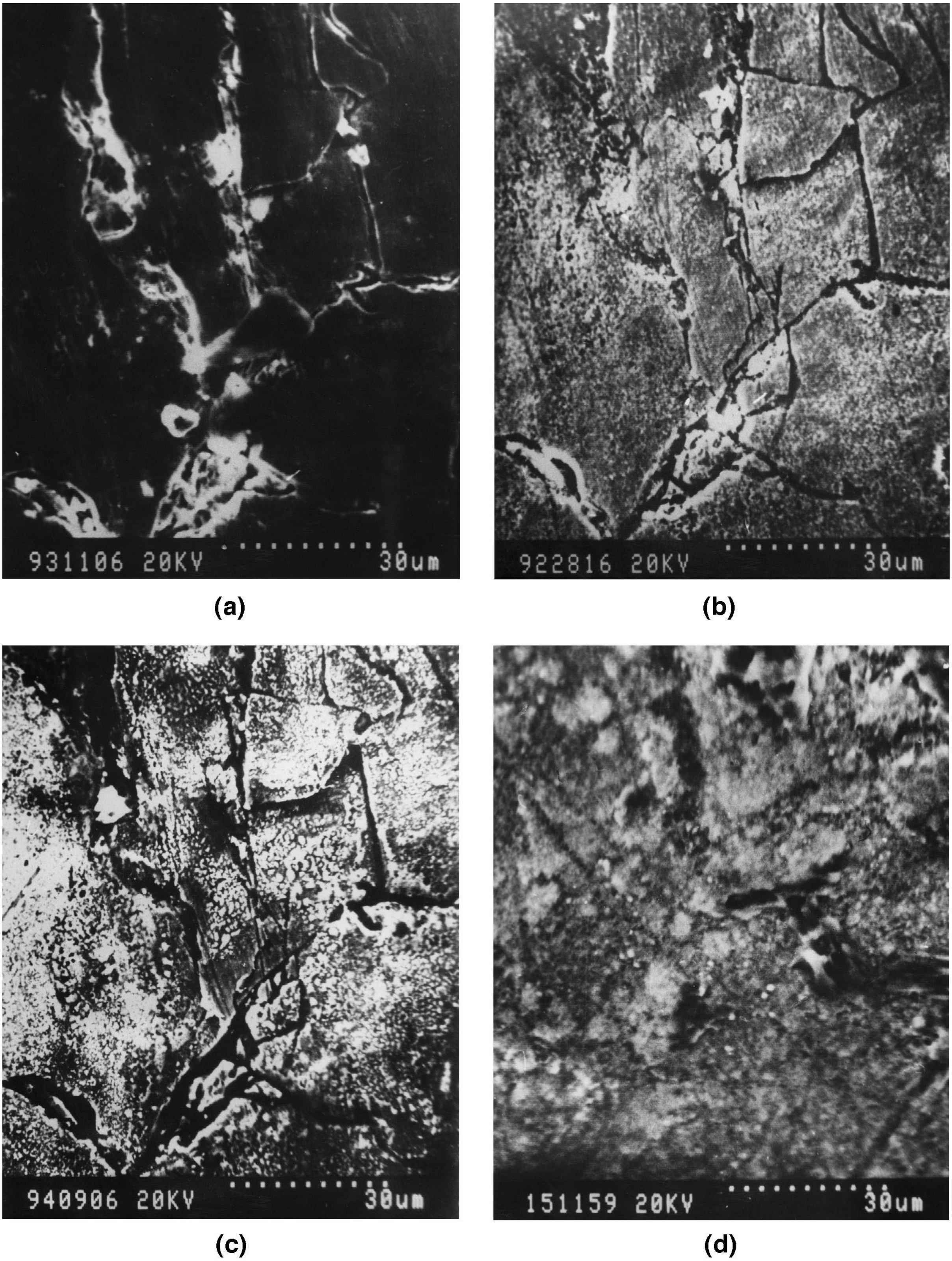
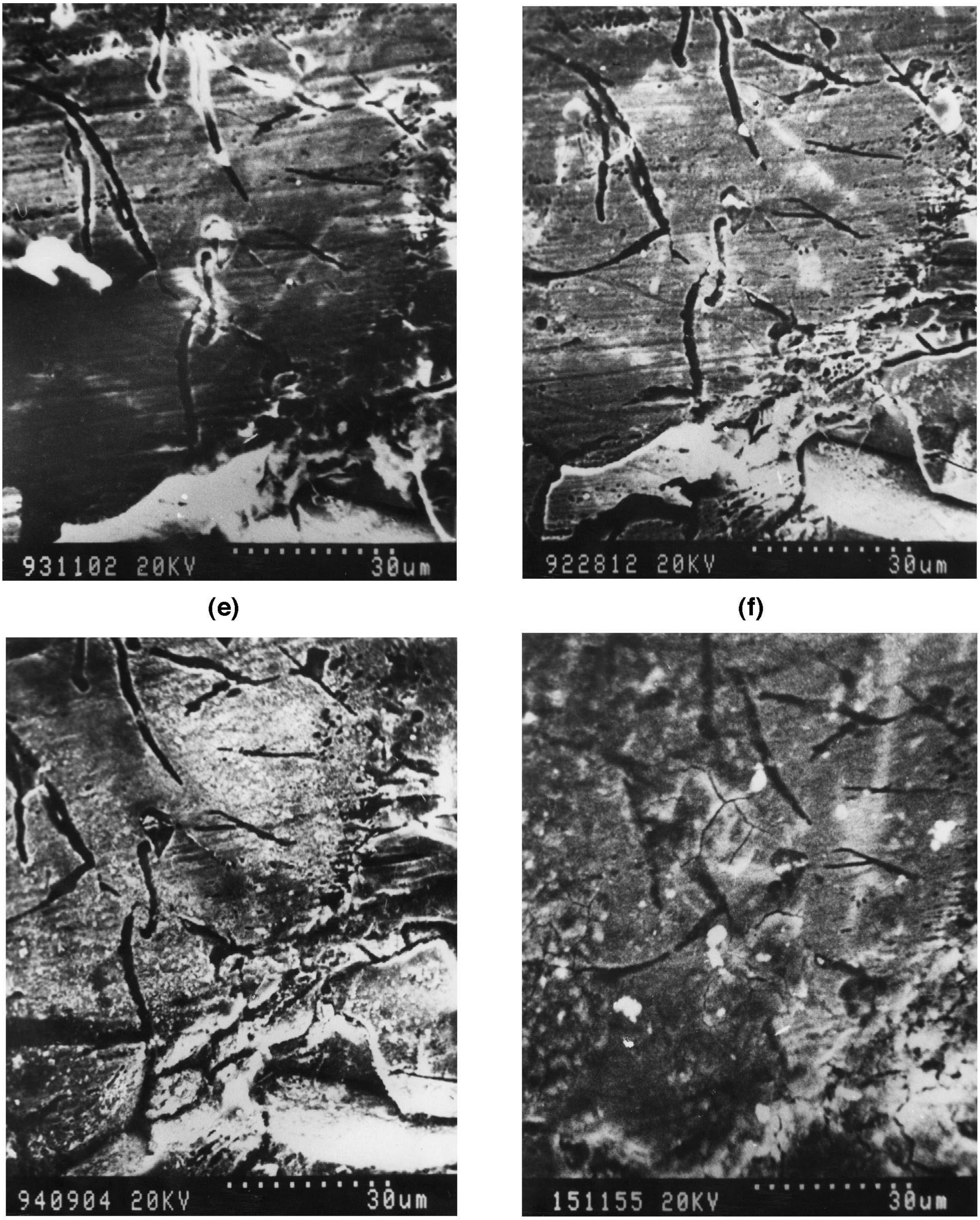


Fig. 1. Morphologies of the WEs in H_2 and O_2. (a) 0 h (in H_2); (b) 10 h (H_2); (c) 100 h (H_2); (d) 200 h (H_2); (e) 0 h (in O_2); (f) 10 h (O_2); (g) 100 h (O_2); (h) 200 h (O_2).

The WEs were cathodically charged with a current of 0.4 mA by the galvanostat of PARC M273, and the potentials of WEs were measured. The WEs were taken out of the system after 10 h, 100 h and 200 h of charging, respectively, first immersed in a dilute solution of H_3BO_3 for neutralization, then washed with tap water. After being



(e) **(f)**

(g) **(h)**

Fig. 1. (*continued*)

Table 1
Relations of potentials (φ) and duration of cathodic polarization (t)

t/h		1	10	20	40	100	150	200
φ/V (vs. Hg/HgO)	in H_2	−1.056	−1.064	−1.060	−1.070	−1.063	−1.062	−1.061
	in O_2	−0.779	−0.782	−0.781	−0.790	−0.778	−0.780	−0.783

dried, the morphologies and the average surface compositions of specific areas of the sample were determined.

The negative electrodes of AA size MH/Ni batteries with a rated capacity of 1.2 Ah were made of powdered active materials of the above composition with a particle size less than 74 μm. They were taken out of the batteries after 250 cycles. The scheme for each cycle consisted of a charge with 1 C for 1.5 h, a pause for 10 min, and a discharge with 1 C to 1.0 V. These negative electrodes were washed with 0.5 M EDTA solution at 90±5°C for 2 h, with the pH value of the solution constantly adjusted with a solution of NH_4OH–NH_4Cl to 10. Then the solution was filtered and collected. Washing and filtering were repeated once. All the filtrates were collected together and diluted with distilled water to 500 ml. The contents of Ni^{2+} and La^{3+} (usually in the Mm) in the diluted solution were determined by ICP. Because the foamed nickel sheet as the current collector used in negative electrodes also contributed some nickel oxides, the sheet with the same dimension and weight as in the electrodes was tested and examined as above. The amount of oxidized Ni during cycling was obtained by subtracting the Ni^{2+} obtained from foamed Ni sheet from the total content of Ni^{2+} in the filtrates.

3. Results and discussion

3.1. Morphologies of the WEs

Experimental results are shown in Fig. 1.

Fig. 1a–d shows that in H_2 atmosphere WEs expanded evidently, the surfaces were corroded seriously, and the pits were obvious on the surface after 10 h of charging. Intergranular boundaries were thickened after 100 h of charging, and the area of smooth surface reduced remarkably.

Fig. 1e–h shows that the changes of electrode surface in O_2 atmosphere were much less than that in H_2 atmosphere within the same time of charging. Although the intergranular boundaries were thickened slightly, the surface of WEs were still smooth. Therefore we believe that the main causes for the degradation of WEs are the increase of internal stress, the expansion of crystal lattice and the preferential dissolution of Mm in a charged state, rather than the oxidation of the alloy by oxygen.

3.2. Potentials of the WEs

Experimental results are shown in Table 1.

Experimental data showed that potentials of the WEs were about −1.06 V in H_2 and −0.78 V in O_2. In comparison with the results in Section 3.1 and the more negative potential in a charged state in H_2 atmosphere, it may be concluded that the WEs are not much more resistant to corrosion in H_2 atmosphere, than that in O_2 atmosphere, even though the WEs should be protected at more negative potentials in H_2 atmosphere.

3.3. Chemical composition of the WEs

Experimental results are shown in Table 2.

It can be seen from the data that the contents of Mm on the surface rapidly decreased with the duration of charging in H_2 atmosphere, and rather slowly in O_2 atmosphere, as shown in Fig. 2.

Table 2 also shows that the ratio of La/Mm is rather constant in the range of 0.276 to 0.320, with small fluctuations in both atmospheres, thus the content of La

Table 2
Chemical composition of the WEs in H_2 and O_2 atmospheres

%	Ni		Co		Mn		Al		La		Ce		Pr		Nd		Mm		La/Mm	
t/h	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2
0	57.90	56.63	12.67	12.20	6.36	6.74	4.41	5.45	5.67	5.31	9.55	9.24	1.14	0.82	2.30	3.10	18.66	18.98	30.4	28.0
10	60.16	58.15	12.61	12.50	6.79	6.93	3.46	3.52	5.27	5.21	8.30	9.65	0.70	0.99	2.70	3.05	16.97	18.90	31.1	27.6
100	65.14	59.76	14.37	12.89	5.44	6.87	3.45	2.69	3.49	5.19	5.77	8.92	0	0.68	2.34	3.00	11.60	17.79	30.1	29.2
200	65.62	60.42	17.13	13.15	7.42	6.60	1.00	2.61	2.83	4.83	4.04	8.82	0	0.59	1.96	2.98	8.83	17.22	32.0	28.0

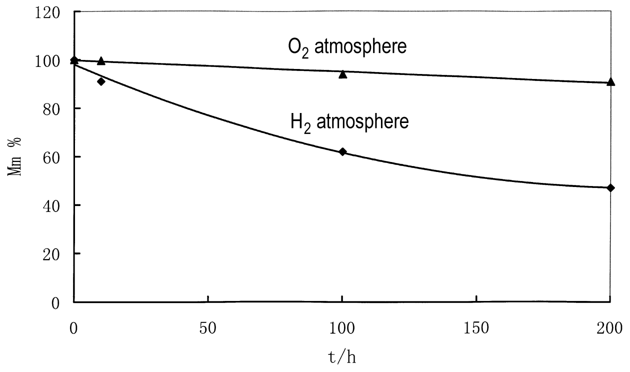


Fig. 2. Relations of contents of Mm and charging time.

might be used for that of Mm in negative electrodes in approximation.

3.4. Contents of Ni^{2+} and La^{3+} in negative electrodes of AA size batteries after 250 cycles

The results are shown in Table 3.

Initially the ratio of Ni and La was Ni/La=57.9/5.67=10.21. Actually, the ratio of the oxidized Ni and La was Ni/La=0.674/0.620=1.09. These results indicated that the Mm contained in the negative electrode was oxidized preferentially during cycling.

Table 3
Oxidation amounts of Ni and La

Content	in grams	in mol$\times 10^{-3}$
Ni^{2+} in filtrate	0.0438	0.744
La^{3+} in filtrate	0.0861	0.620
Ni^{2+} in foamed nickel sheet	0.0042	0.071
Ni actually oxidized	0.0396	0.674

4. Conclusion

Pieces of nonpulverized Mm alloy electrodes were used as WEs in this experiment so that the surface morphologies can be observed and the surface composition of the WEs at specific spots on the surface can be determined.

The increase of internal stress of the alloy ($MmNi_{3.55}La_{0.75}Mn_{0.4}Al_{0.3}$), the expansion of crystal lattice and the dissolution of Mm preferentially during charging are believed to be the causes for the degradation of the alloy hydride. This result was accordant with that of the ICP analysis of the EDTA solution extracts of negative electrodes from AA-size Ni/MH batteries after 250 cycles of charging and discharging.

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