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Investigation on the Corrosion Resistance of $V_3TiNi_{0.56}M_x$ Hydrogen Storage Alloy in Alkaline Solution

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Abstract: Vanadium-based hydrogen storage alloys are easily corroded in KOH solution, which leads to their poor electrochemical cyclic durability in alkaline solution and limits their application in the Ni/MH battery. In this paper, the structure transformation of $V_3TiNi_{0.56}M_x$ alloys during full immersion corrosion in alkaline solution was investigated; the corrosion potentials, the Tafel curves and the impedance spectra were tested for the $V_3TiNi_{0.56}M_x$ alloys in alkaline solution. The results show that the corrosion of $V_3TiNi_{0.56}M_x$ alloys in alkaline solution is caused by the continuous dissolve of the TiNi compound based phase as a micro-current collector, and the addition of alloy elements Cr and Al can prevent the dissolve of TiNi compound based phase, shift the alloy corrosion potential and improve the corrosion resistance of alloys in alkaline solution.

Key Words: vanadium-based hydrogen storage alloy; Ni/MH battery; corrosion resistance

Vanadium-based solid solution alloys are known to have a large hydrogen storage capacity and easy activation as a new type of hydrogen storage materials, and have been considered as a promising candidate for negative electrode of Nickel/Metal Hydride (Ni/MH) batteries[1,2]. However, there had been no literature available on the application of vanadium-based solid solution alloys in Ni-MH battery because of their poor cyclic stability in KOH electrolyte solution. In order to research the corrosion behavior of the $V_3TiNi_{0.56} M_x$ (M=Al, Cr; x=0.1,0.3) alloys in alkaline solution, the microstructure transformation of alloys during full immersion corrosion in alkaline solution has been investigated, the corrosion potentials, the Tafel curves and impedance spectra of the alloys have been tested.

1   Experimental

1.1   Alloy preparation and microstructure observation

First, the $V_3TiNi_{0.56}M_x$(M=Al, Cr; x=0.1, 0.3) alloys were synthesized by means of Self-propagating High-temperature Synthesis (SHS), using V_2O_5, TiO_2, Al, Cr and Ni powders as raw materials[3], then the obtained alloys were melt several times in a vacuum induction furnace to make their composition pure and homogeneous, and cast into button shape ingots, and at last, the alloy ingots were cut into experimental samples of square pieces. The structure transformation of alloys during the period of full immersion corrosion in alkaline solution was observed by optical microscope. The alloy $V_3TiNi_{0.56}Cr_{0.3}$ was also examined by scanning electron microscopy (SEM) in order to determine the distribution of elements in the alloys. The phases of alloy were analyzed by X-ray diffraction of typed D/MAX-1200.

1.2   Immersing corrosion experiments of alloys in KOH solution

Before immersed into alkaline solution, first, the oxides on the surface of alloy samples were removed using sand-papers; then, the tested surface of the alloy samples were polished and cleaned using distillation water and alcohol. The alloy samples were fully immersed into 6 mol/L KOH solution for 240 h at room temperature. The structure of the immersed alloy samples was observed once at an interval of 40 h during the

immersing corrosion experiments.

1.3 Electrochemical measurement

Before electrochemical measurement, the alloy sample to be measured must be made into an alloy electrode called working electrode. For electrical contact, a copper wire was welded on the surface of the alloy sample; and then another alloy sample surface selected to be observed was polished; at last, all the alloy sample surfaces, except the surface selected to be observed, were covered with colophony; thus the alloy sample became an alloy electrode. The alloy electrode was used as a working electrode, a sintered Ni(OH) /NiOOH electrode was used as counter electrode, a Hg/HgO electrode was used as a reference electrode; all constituted a three electrodes electrochemical testing system together with 6 mol/L KOH aqueous solution and an electrochemical instrument of Autolab. The experiments were performed at 25 °C. The alloy electrodes were polarized at a –1.2 V voltage for 180 sec before electrochemical measurement in order to remove the oxide film on the observed surface. The Tafel curves of the alloy electrodes were recorded from –1.4 V to –0.2 V with a scanning speed of 0.001 V/s. The impedance spectra of alloy electrodes were measured from 10 kHz to 0.5 mHz at a amplitude of perturbation 5 mV to the electrodes under open-circuit condition [4]. The alloy electrodes were charged at 100 mA/g for 3 h and discharged at 50 mA/g to –0.6 V (vs. Hg/HgO); after each charging and discharging process the alloy electrodes were rested for 30 min.

2 Results and discussion

2.1 Phase analysis of alloys

Fig.1 shows the X-ray diffraction patterns of $V_3TiNi_{0.56}M_x$ alloys containing different amount of Al and Cr element. According to the XRD analysis, every alloy sample is found to consist of two basic phases: a vanadium-based solid solution main phase and a TiNi compound-based secondary phase. The TiNi compound-based phase precipitated along the grain boundary to form a three-dimensional network. A AlV_3 phase was also found when the alloy sample contained Al element. The XRD patterns also show that the peaks of the main phase and the secondary phase shifted to higher angle with increasing the Al and Cr content, respectively, which indicated that the lattice constants of the alloys were reduced as the Al and Cr content increased.

2.2 SEM and energy spectrum analysis of alloys

SEM image of the $V_3TiNi_{0.56}Cr_{0.3}$ alloy is shown in Fig.2. The $V_3TiNi_{0.56}Cr_{0.3}$ alloy consisted of vanadium-based solid solution main phase (gray) and TiNi compound-based secondary phase (white); in addition, some black holes were also found in the alloy. The chemical composition of grain boundary and grain inner of the $V_3TiNi_{0.56}Cr_{0.3}$ alloy is shown in Table.1. It is indicated that the grain inner mainly contained V and Ti elements while the grain boundary contained V, Ti,
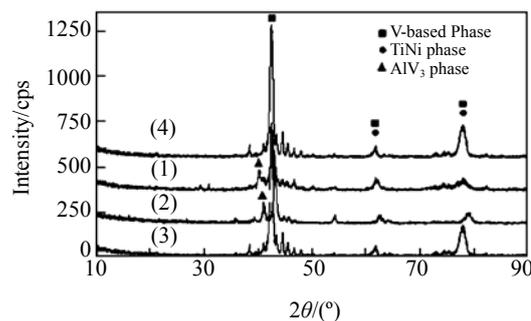
Fig.1 XRD patterns of $V_3TiNi_{0.56}M_x$ alloys:
(1) $V_3TiNi_{0.56}Al_{0.1}$, (2) $V_3TiNi_{0.56}Al_{0.3}$,
(3) $V_3TiNi_{0.56}Cr_{0.1}$, and (4) $V_3TiNi_{0.56}$-$Cr_{0.3}$
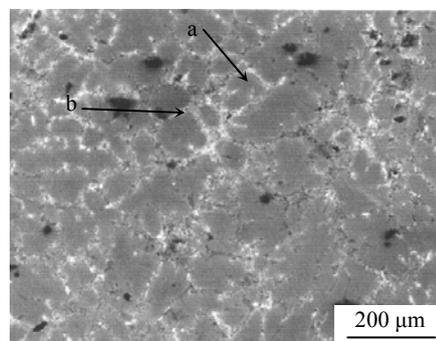
Fig.2 SEM image of the $V_3TiNi_{0.56}Cr_{0.3}$ alloy:
(a) grain inner and (b) grain boundary

Table 1 Elements distribution in micro-zone of Fig.2 for $V_3TiNi_{0.56}Cr_{0.3}$ alloy (at%)

Elements	Grain inner	Grain boundary
Cr	1.76	6.91
V	73.23	62.38
Ti	18.93	15.77
Si	0.41	0.54
Ni	5.67	14.40

and Cr elements. The alloy elements Ni and Cr were mainly distributed along the grain boundary. It was also easily concluded that the atomic ratio of Ti and Ni in the grain boundary was close to 1:1, which proved that the grain boundary phase was mainly TiNi compound.

2.3 Microstructure transformation during the immersing corrosion test

Fig.3 and Fig.4 show the microstructure transformation of the $V_3TiNi_{0.56}Al_{0.3}$ and $V_3TiNi_{0.56}Cr_{0.3}$ alloys, respectively, which were immersed fully in 6 mol/L KOH solution for different time. From Fig.3 and Fig.4, it was found that the grain boundary of the alloys was not observed on the polished surface after the alloy samples immersed in the

alkaline solution for 40 h; the grain boundary appeared after 120
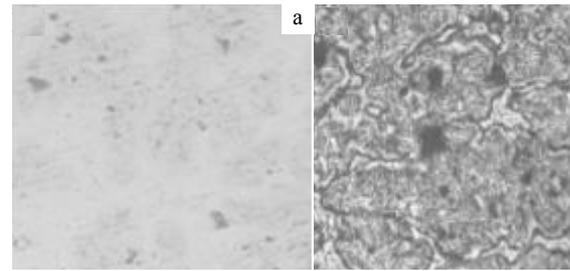
Fig.3 Optical micrographs of the $V_3TiNi_{0.56}Al_{0.3}$ alloy after different immersing time:
(a) 40 h, (b) 120 h, and (c) 160 h
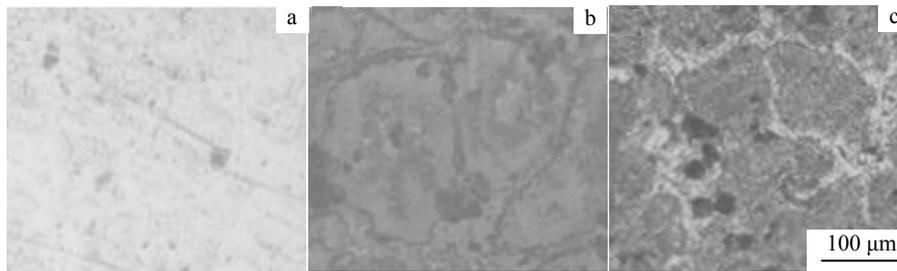
Fig.4 Optical micrographs of the $V_3TiNi_{0.56}Cr_{0.3}$ alloy after different immersing time: (a) 40 h, (b) 120 h, and (c) 160 h

h but was not continuous; the grain boundary became more wider and could be observed clearly after 160 h. By comparing Fig.3 and Fig.4, it is not hard to find that the micrograph of $V_3TiNi_{0.56}Al_{0.3}$ had more grain boundaries than that of $V_3TiNi_{0.56}Cr_{0.3}$. According to the above tests, it is concluded that the TiNi compound-based phase was more easily to be corrosive than the vanadium-based solid solution main phase in KOH solution. The corrosion resistance of $V_3TiNi_{0.56}Cr_{0.3}$ alloy was better than that of $V_3TiNi_{0.56}Al_{0.3}$ in alkaline solution.

2.4　Measurement of Tafel curve

Fig.5 and Fig.6 show the Tafel curves of the $V_3TiNi_{0.56}M_x$ alloys contained different amounts of Al and Cr elements. Generally speaking, the corrosion resistance of alloys is improved with the corrosion potential ascending[4]. The corrosion potential of $V_3TiNi_{0.56}Al_x(x=0.1, 0.3)$ increased from −0.872 to −0.758 V with increasing the content of Al element. The same phenomenon appeared in $V_3TiNi_{0.56}Cr_x(x=0.1, 0.3)$, i.e. when the content of Cr ascended from 0.1 to 0.3, the corrosion potential increased from −0.861 to −0.743 V. The corrosion potential of $V_3TiNi_{0.56}Al_x$ was smaller than that of $V_3TiNi_{0.56}Cr_x$ when the same amount of Al and Cr elements were added into the alloys. It is also proved that the alloy $V_3TiNi_{0.56}Cr_{0.3}$ has better corrosion resistance than $V_3TiNi_{0.56}Al_{0.3}$ in KOH solution.

2.5　Measurement of impedance spectra

The Nyquist plots of impedance spectra are shown in Fig.7 for the electrodes made from the $V_3TiNi_{0.56}M_x$ alloys. According to Kuriyama's theory[5], the Nyquist plots of all alloy electrodes consist of a small semi-circle located in high frequency zone, a large semi-circle located mainly in medium frequency zone and an oblique line situated in low frequency range. The small semi-circle in high frequency zone is related to the contact resistance among alloy particles, alloy powders and electric current agents. The large semi-circle in medium and high frequency zones represents the surface electric current im
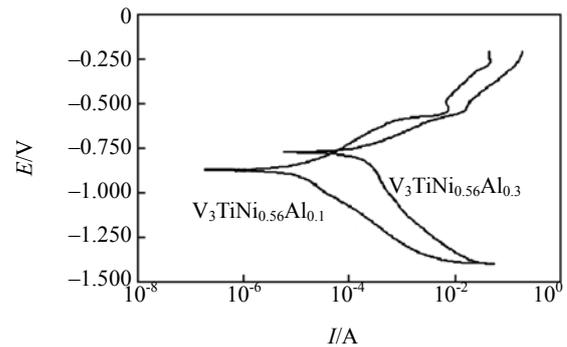
Fig.5 Tafel curves of $V_3TiNi_{0.56}Al_x(x=0.1, 0.3)$

Fig.6　Tafel curves of $V_3TiNi_{0.56}Cr_x(x=0.1, 0.3)$
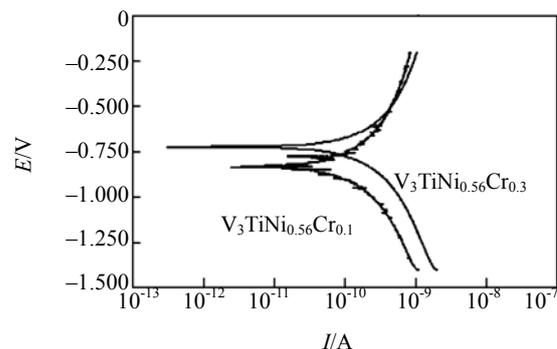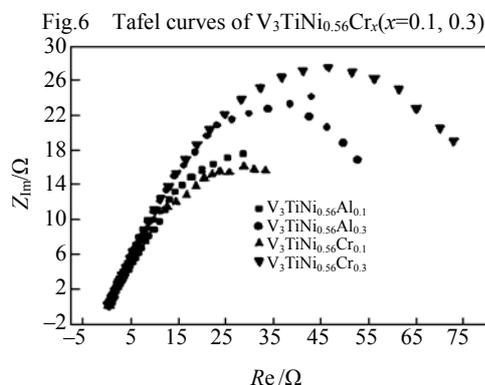
Fig.7　Nyquist plots of impedance spectra for the electrodes

pedance of alloy electrodes. The oblique line in low frequency range indicates the resistance of hydrogen diffusion in alloy electrodes. According to Fig.7, the radii of the large and small semi-circles increase as the increasing of Al or Cr content in the alloys, indicating the increase of the electrochemical resistance of the alloys. The change of small semi-circle radius proved the corrosion of the TiNi compound-based phase in KOH solution, leading to broadening of the grain boundary and increasing of hydrogen diffusion resistance in the alloy. The increase of large semi-circle radius indicated that the vanadium on the alloy surface was dissolved into the KOH solution, causing the decrease of hydride formation elements in the hydrogen storage alloys.

3　Conclusions

$V_3TiNi_{0.56}M_x$ (*M*=Al, Cr; *x*=0.1, 0.3) alloys mainly consist of two phases: a vanadium-based solid solution main phase and a TiNi compound-based second phase. The AlV_3 phase also appear when Al is added into the alloys. The alloy elements Al and Cr are predominantly distributed in the grain boundary.

The results of immersing corrosion experiments of $V_3TiNi_{0.56}M_x$ (*M*=Al, Cr; *x*=0.1, 0.3) alloys in KOH solution show that the dissolving of TiNi compound-based phase into KOH solution leads to the corrosion of alloys. The corrosion resistance of $V_3TiNi_{0.56}Cr_{0.3}$ alloy is better than that of $V_3TiNi_{0.56}Al_{0.3}$ alloy. The alloy corrosion potentials increase as the contents of alloy elements Al or Cr increase, proving that the alloy elements Al and Cr can improve the corrosion resistance of $V_3TiNi_{0.56}M_x$ (*M*=Al, Cr; *x*=0.1, 0.3) alloys in KOH solution. These facts were also revealed by the electrochemical impedance spectra measurements of the alloy.

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贮氢合金 $V_3TiNi_{0.56}M_x$ 耐腐蚀性能研究

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摘　要：钒基固溶体贮氢合金在 KOH 电解质溶液中容易腐蚀，导致合金的电化学循环稳定性差，限制了钒基固溶体贮氢合金在 Ni/*M*H 电池中的应用。通过测试贮氢合金 $V_3TiNi_{0.56}M_x$(*M*=Al、Cr; *x*=0.1、0.3)在 KOH 溶液浸泡过程中组织结构变化和腐蚀电位、交流阻抗谱等，研究了钒基固溶体贮氢合金 $V_3TiNi_{0.56}M_x$ 的耐碱液腐蚀性能。结果表明：钒基固溶体贮氢合金在碱液中的腐蚀原因是作为导电集流体的 TiNi 第二相在 KOH 溶液中的不断溶解；在合金 $V_3TiNi_{0.56}$ 中添加 Al 和 Cr 元素，可阻止合金中分布于晶界的 TiNi 第二相的溶解，使合金的腐蚀电位提高，从而提高钒基固溶体贮氢合金的耐碱液腐蚀能力。

关键词：钒基贮氢合金；Ni/*M*H 电池；耐腐蚀性能

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